# Journal of
# Inorganic & Nuclear Chemistry

VOLUME 12 1960

Vol.
12
59/60

EDITORS

JOSEPH J. KATZ, Argonne · A. G. MADDOCK, Cambridge · L. E. J. ROBERTS, Harwell · E. J. W. VERWEY, Eindhoven

EDITORIAL ADVISORY BOARD

*U.S.A.:* L. F. AUDRIETH and JOHN C. BAILAR JR., Univ. of Illinois · E. O. BRIMM, Linde Air Products · HERBERT C. BROWN, Purdue · ANTON B. BURG, Univ. South Calif. · CHARLES D. CORYELL, M.I.T. and R. W. DODSON, Brookhaven · W. CONARD FERNELIUS, Penn. State Univ. WARREN C. JOHNSON, Chicago · JACOB KLEINBERG, Univ. of Kansas · K. A. KRAUS, Oak Ridge · W. F. LIBBY, Los Angeles · W. M. MANNING, Argonne · THERALD MOELLER, Univ. of Illinois · EUGENE G. ROCHOW, Harvard · H. I. SCHLESINGER, Chicago WALTER C. SCHUMB, M.I.T. · GLENN T. SEABORG, Univ. of California · P. W. SELWOOD, Evanston · F. H. SPEDDING, Ames · R. W. STOUGHTON, Oak Ridge · DON M. YOST, Pasadena, Calif. · W. H. ZACHARIASEN, Chicago · R. A. PENNEMAN and B. B. CUNNINGHAM, Univ. of California · H. TAUBE, Chicago

*U.K. and Commonwealth:* J. S. ANDERSON, F.R.S., Melbourne · C. C. ADDISON, Nottingham C. B. AMPHLETT, Harwell · F. M. BREWER, Oxford · G. E. COATES, Durham H. J. EMELÉUS, F.R.S., Cambridge · F. FAIRBROTHER, Manchester · H. M. N. H. IRVING, Oxford · L. E. ORGEL, Cambridge · A. R. POWELL, F.R.S., Wembley · P. L. ROBINSON, Newcastle-upon-Tyne · R. SPENCE, Harwell · H. G. THODE, F.R.S., Hamilton · L. YAFFE, Montreal

*Austria:* E. BRODA, Vienna · BERTHA KARLIK, Vienna · V. GUTMANN, Vienna

*Denmark:* J. BJERRUM, Copenhagen

*France:* J. BÉNARD, Paris · J. CHÉDIN, Paris · J. GUÉRON, Paris · M. MAGAT, Paris

*Germany:* W. HIEBER, Munich · G. JANDER, Berlin · A. MUENSTER, Frankfurt

*Netherlands:* A. E. VAN ARKEL, Leiden · A. H. W. ATEN JR., Amsterdam J. H. DE BOER, Geleen · J. H. VAN SANTEN, Eindhoven

*Israel:* M. BOBTELSKY, Jerusalem · *Italy:* V. CAGLIOTI, Rome

*Norway:* H. HARALDSEN, Oslo · ODD HASSEL, Oslo

*Persia:* H. A. C. McKAY, Tehran

*Sweden:* G. HÄGG, Uppsala · L. G. SILLÉN, Stockholm

*Switzerland:* G. SCHWARZENBACH, Zürich

PERGAMON PRESS NEW YORK • LONDON • PARIS • LOS ANGELES

# JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY

*Editors:*

JOSEPH J. KATZ: *Argonne National Laboratory, Box 299, Lemont, Illinois, U.S.A.*
A. G. MADDOCK: *University Chemical Laboratory, Lensfield Road, Cambridge, England*
L. E. J. ROBERTS: *Atomic Energy Research Establishment, Harwell, Didcot, Berks, England*
E. J. W. VERWEY: *Philips Research Laboratories, Eindhoven, The Netherlands*

## NOTES FOR CONTRIBUTORS

### I. General

1. Papers should, in general, be concerned with original work in the field of inorganic and nuclear chemistry. They should be submitted to the Editors, Dr. A. G. MADDOCK, Dr. L. E. J. ROBERTS, or Dr. J. J. KATZ, or, in the case of papers not in the English language, to Dr. E. J. W. VERWEY. The addresses are given above.

2. Fifty free reprints of each paper are supplied. Additional copies can be supplied at a reasonable cost if ordered at the time when the first proofs are returned. A reprint order form will accompany proofs.

### II. Script Requirements

1. Scripts should be submitted in duplicate. They must be typewritten, and double-spaced. Authors are requested to make clear any greek characters which may be confused with ordinary letters or with other characters. Authors will receive proofs for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, where the amount of alteration makes it advisable.

2. Illustrations should be placed at the end of the manuscript, and legends should be typed on a separate sheet. It is requested that photographs should be kept to the minimum necessary. Line drawings or good photo-prints may be provided. Line drawings must include all relevant details: if they are already well drawn it may be possible to reproduce them direct from the original. It is not possible to reproduce from "dye-line" prints, or from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. Any lettering on diagrams—other that Greek letters, symbols, etc.—should be stencilled and should be sufficiently large and bold to permit reproduction when the diagram has been reduced to a size suitable for inclusion in the journal.

3. References should be clearly indicated in the text by superior numbers. Full references should be given in numbered footnotes containing author's name, initials, title of paper (where desired), abbreviated title of journal, year, volume number, and page number.

4. The text of articles submitted must be concise and in a readily understandable style. The technical description of the methods used should only be given in detail when such methods are new. The essential contents of each paper should be briefly recapitulated in an abstract. French and German papers should be submitted with English abstracts. **Four copies of the English abstracts are required with all papers, including those in the English language.**

5. To conserve space, authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc.) for printing in smaller type.

PERGAMON PRESS INC,

122 EAST 55TH STREET, NEW YORK 22, N.Y. 4 & 5 FITZROY SQUARE, LONDON W.1

Vol
12
1959/

# LIST OF CONTENTS

## NUMBERS 1/2


R. P. SCHUMAN and P. GORIS: Half-life and decay of niobium-94 . . . . . 1
G. HARBOTTLE: Half-lives of $^{208}$Tl, RaD and $^{207}$Bi . . . . . 6
J. E. GINDLER and R. K. SJOBLOM: Electron-capture/negatron-emission branching ratio of $^{236}$Np (22 hr) . . . . . 8
H. R. HEYDEGGER and P. K. KURODA: Natural occurrence of the short-lived barium and strontium isotopes . . . . . 12
K. E. SIEKIERSKA, A. SOKOLOWSKA and I. G. CAMPBELL: Reactions of neutron-activated arsenic atoms in organic media—I. Formation of phenyl arsenic compounds during neutron irradiation of arsenic trichloride in benzene . . . . . 18
P. G. HANSEN: The conditions of electrodeposition of insoluble hydroxides at a cathode surface: A theoretical investigation . . . . . 30
RAM SAHAI SAXENA and C. S. BHATNAGAR: Electrometric studies on silver arsenites . . . . 38
B. R. CURRELL, M. J. FRAZER, W. GERRARD, E. HAINES and L. LEADER: Some replacement reactions on silicon and sulphur (IV) atoms . . . . . 45
T. MOELLER and E. P. HORWITZ: Observations on the rare earths—LXX. Some characteristics of ethylenediaminetetraacetic acid, N-hydroxyethylethylenediaminetriacetic acid, and 1,2-diaminocyclohexanetetraacetic acid chelates of certain rare-earth metal ions . . . . . 49
D. F. PEPPARD, J. R. FERRARO and G. W. MASON: The preparation, physical properties and infra-red spectra of several new organophosphonates . . . . . 60
D. C. BRADLEY, AMAR K. CHATTERJEE and AMIYA K. CHATTERJEE: Sexavalent compounds of uranium—I. Uranyl alkoxides and uranium hexa-alkoxides . . . . . 71
E. RICHARDSON: Some studies on tungstic acid prepared by ion exchange . . . . . 79
J. D. HEFLEY, D. M. MATHEWS and E. S. AMIS: The preparation, preservation and separation of uranium tetrachlorides and uranyl chloride in water, ethanol and water–ethanol solvents . . 84
H. C. MANDELL, JR. and G. BARTH-WEHRENALP: Ammonolysis of perchchoryl fluoride . . 90
J. VAN R. SMIT, J. J. JACOBS and W. ROBB: Cation exchange properties of the ammonium heteropolyacid salts . . . . . 95
J. VAN R. SMIT, W. ROBB and J. J. JACOBS: Cation exchange on ammonium molybdophosphate—I. The alkali metals . . . . . 104
H. J. BORCHARDT: Observations on reactions of uranium compounds . . . . . 113
N. C. LI, A. LINDENBAUM and J. M. WHITE: Some metal complexes of citric and tricarballylic acids 122
S. SIEKIERSKI: Extraction from solutions of perchloric acid by tributylphosphate—I. Partition coefficients for zirconium, thorium, cerium, promethium and yttrium . . . . . 129
G. F. BEST, E. HESFORD and H. A. C. MCKAY: Tri-n-butyl phosphate as an extracting agent for inorganic nitrates—VII. The trivalent actinide nitrates . . . . . 136
D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and S. MCCARTY: Application of phosphoric acid esters to the isolation of certain *trans*-plutonides by liquid–liquid extractions . . . . . 141
D. GRDENIĆ and B. KORPAR: The complexing of tetravalent uranium with dialkylpyrophosphoric acid . . . . . 149
J. M. FLETCHER, P. G. M. BROWN, E. R. GARDNER, C. J. HARDY, A. G. WAIN and J. L. WOODHEAD: Nitrosylruthenium nitrato complexes in aqueous nitric acid . . . . . 154
M. TAUBE: The influence of diluent polarity on extraction of plutonium complexes to organic media 174
T. C. FRANKLIN and H. V. SEKLEMIAN: A study of solutions of titanium of low oxidation states . 181
H. J. MATSUGUMA and L. F. AUDRIETH: The stability of aqueous solutions of hydroxylamine-*O*-sulphonic acid . . . . . 186
J. KENNEDY and R. V. DAVIES: The adsorption of inorganic salts by amine resins from organic solvents . . . . . 193
Book Review:
"The Transuranium Elements" by GLENN T. SEABORG (reviewed by JAMES W. COBBLE) . . . 199


## NUMBERS 3/4


K. WOLFSBERG, D. R. NETHAWAY, H. P. MALAN and A. C. WAHL: Identification of $^{142}$Xe and measurement of its cumulative yield from thermal-neutron fission of $^{235}$U . . . . . 201
J. E. SATTIZAHN, J. D. KNIGHT and M. KAHN: Short-lived bromine and selenium nuclides from fission . . . . . 206
J. A. MARINSKY and E. EICHLER: A new fission product: $^{74}$Ga . . . . . 223
L. R. BUNNEY, J. O. ABRIAM and E. M. SCADDEN: Half-lives of $^{148}$Pm and $^{151}$Pm . . . . . 228
F. P. BRAUER, R. W. STROMATT, J. D. LUDWICK, F. P. ROBERTS and W. L. LYON: The specific activity and half-life of $^{237}$Np . . . . . 234
K. S. TOTH and J. O. RASMUSSEN: Two new neutron-deficient terbium activities . . . . . 236
J. F. TATE and M. M. JONES: The use of electrical conductivity data with Job's method . . . . 241
H. J. BORCHARDT: Initial reaction rates from DTA . . . . . 252
H. G. HEAL: "Onium" base borohydrides—I. Trimethyl sulphonium borohydride . . . . 255
T. MOELLER and V. GALASYN: Observations on the rare earths—LXXI. Chemical and electrochemical studies of iodide systems in anhydrous N:N′-dimethylformamide . . . . . 259
R. R. HOLMES: An examination of the basic nature of the trihalides of phosphorus, arsenic and antimony . . . . . 266
W. W. WENDLANDT and J. L. BEAR: Thermal decomposition of the heavier rare-earth metal nitrate hydrates. Thermobalance and differential thermal analysis studies . . . . . 276



Vol.
12
59/60

L. H. Sutcliffe and J. R. Weber: The species of Co(III) present in aqueous perchloric acid solutions 281
Y. Marcus: The anion exchange of metal complexes—IV. The iron(III)—chloride system . . 287
A. M. Lefevre, J. F. Lefevre et A. Raggenbass: Dosage radiochimique du césium par colorimétrie de la dipicrylamine . . . . . 297
P. R. Gray: Separation of cesium from fission product waste solutions . . . . . 304
R. A. Zingaro and J. C. White: The extraction of nitric acid and thorium nitrate by tri-n-octylphosphine oxide in cyclohexane . . . . . 315
W. E. Keder, J. C. Sheppard and A. S. Wilson: The extraction of actinide elements from nitric acid solutions by tri-n-octylamine . . . . . 327
C. G. Warren and J. F. Suttle: Solvent extraction of scandium, yttrium and lanthanum by the monoalkyl orthophosphoric acids . . . . . 336
Notes:
E. Schulek, E. Körös and L. Maros: The dialysis of polysulphide solutions . . . . . 343
A. G. Wain, P. G. M. Brown and J. M. Fletcher: The separation and estimation of nitro and non-nitro (nitrato) complexes of nitrosylruthenium in nitric acid solution by paper chromatography 346
E. Richardson: Molybdic acid and its organic complexes—III. Some studies on the acid nature molybdic oxide and its solubility in polyhydroxy alcohols . . . . . 349
M. T. Beck and S. Görög: On the protonation of complexes . . . . . 353
E. L. Muetterties: Synthesis of alkali metal tetrachloroborates . . . . . 355
V. M. Padmanabhan, S. C. Saraiya and A. K. Sundaram: Thermal decomposition of some oxalates . . . . . 356
A. B. Beadle, D. F. Dance, K. M. Glover and J. Milstead: The half-life of americium-243 359
H. A. Rutter, Jr. and J. D. McQueen: Synthesis of $^{52}$Mn and $^{76}$As labelled phthalocyanines . 361
G. Curthoys and J. H. Green: The polarographic behaviour of some square complex compounds of platinum . . . . . 363
J. Krtil and V. Kouřim: Exchange properties of ammonium salts of 12-heteropoly-acids. Sorption of caesium on ammonium phosphotungstate and phosphomolybdate . . . 367
V. Kouřim: Coprecipitation of carrier-free caesium with 12-heteropolyacids in a strong acid medium . . . . . 370
G. W. Parshall: Synthesis of methyldichlorophosphine and dimethylchlorophosphine . . 372
D. K. Cartwright and E. J. Robbins: A source of error in the determination of uranium-235 by gamma-spectrometry . . . . . 373
A. S. Kertes: Unstable hydration of hydrochloric acid in tri-n-butyl phosphate . . . . 377
H. E. Rauscher, N. Sutin and J. M. Miller: The Szilard–Chalmers reaction in *cis*- and *trans*-dichloro-bis-(ethylenediamine)-cobalt(III) nitrate . . . . . 378
Gerd H. Dahl and Riley Schaeffer: The convenient laboratory preparation of borazole . 380
Letters to the Editor:
Taichi Sato: The decomposition of nitric acid co-extracted with uranyl nitrate into tributyl phosphate . . . . . 382
M. Hillman: The chemistry of decaborane II iodination in solvent . . . . . 383
Announcement . . . . . 385
Erratum: F. A. Cotton and J. W. George: Properties of $SF_4$ and its adduct with $BF_3$. . . . 386

Vol. 12 1959/6

## AUTHOR INDEX

(B denotes Book Review; E denotes Erratum)

Abriam, J. O. p. 228
Amis, E. S. p. 84
Audrieth, L. F. p. 186
Barth-Wehrenalp, G. p. 90
Beadle, A. B. p. 359
Bear, J. L. p. 276
Beck, M. T. p. 353
Best, G. F. p. 136
Bhatnagar, C. S. p. 38
Borchardt, H. J. pp. 113, 252
Bradley, D. C. p. 71
Brauer, F. P. p. 234
Brown, P. G. M. pp. 154, 346
Bunney, L. R. p. 228
Campbell, I. G. p. 18
Cartwright, D. K. p. 373
Chatterjee, Amar K. p. 71
Chatterjee, Amiya K. p. 71
Cobble, J. W. p. 199(B)
Cotton, F. A. p. 386(E)
Currell, B. R. p. 45
Curthoys, G. p. 363
Dahl, G. H. p. 380
Dance, D. F. p. 359
Davies, R. V. p. 193
Driscoll, W. J. p. 141
Eichler, E. p. 223
Ferraro, J. R. p. 60
Fletcher, J. M. pp. 154, 346
Franklin, T. C. p. 181
Frazer, M. J. p. 45
Galasyn, V. p. 259
Gardner, E. R. p. 154
George, J. W. p. 386(E)
Gerrard, W. p. 45
Gindler, J. E. p. 8
Glover, K. M. p. 359
Goris, P. p. 1
Görög, S. p. 353
Gray, P. R. p. 304
Green, J. H. p. 363
Haines, E. p. 45
Hansen, P. G. p. 30
Harbottle, G. p. 6
Hardy, C. J. p. 154
Heal, H. G. p. 255
Hefley, J. D. p. 84
Hesford, E. p. 136
Heydegger, H. R. p. 12
Hillman, M. p. 383
Holmes, R. R. p. 266
Horwitz, E. P. p. 49
Jacobs, J. J. pp. 95, 104
Jones, M. M. p. 241
Kahn, M. p. 206
Keder, W. E. p. 327
Kennedy, J. p. 193
Kertes, A. S. p. 377
Knight, J. D. p. 206
Körös, E. p. 343
Kouřim, V. pp. 367, 370
Krtil, J. p. 367
Kuroda, P. K. p. 12
Leader, L. p. 45
Lefevre, A. M. p. 297
Lefevre, J. F. p. 297
Li, N. C. p. 122
Lindenbaum, A. p. 122
Ludwick, J. D. p. 234
Lyon, W. L. p. 234
Malan, H. P. p. 201
Mandell, Jr., H. C. p. 90
Marcus, Y. p. 287
Marinsky, J. A. p. 223
Maros, L. p. 343
Mason, G. W. pp. 60, 141
Mathews, D. M. p. 84
Matsuguma, H. J. p. 186
McCarty, S. p. 141
McKay, H. A. C. p. 136
McQueen, J. D. p. 361
Miller, J. M. p. 378
Milstead, J. p. 359
Moeller, T. pp. 49, 259
Muetterties, E. L. p. 355
Nethaway, D. R. p. 201
Padmanabhan, V. M. p. 356
Parshall, G. W. p. 372
Peppard, D. F. pp. 60, 141
Raggenbass, A. p. 297
Rasmussen, J. O. p. 236
Rauscher, H. E. p. 378
Richardson, E. pp. 79, 349
Robb, W. pp. 95, 104
Robbins, E. J. p. 373
Roberts, F. P. p. 234
Rutter, Jr., H. A. p. 361
Saraiya, S. C. p. 356
Sato, T. p. 382
Sattizahn, J. E. p. 206
Saxena, R. S. p. 38
Scadden, E. M. p. 228
Schaeffer, R. p. 380
Schulek, E. p. 343
Schuman, R. P. p. 1
Seklemian, H. V. p. 181
Sheppard, J. C. p. 327
Siekierska, K. pp. 18, 129
Sioblom, R. K. p. 8
Smit, J. van R. pp. 95, 104
Sokolowska, A. p. 18
Stromatt, R. W. p. 234
Sundaram, A. K. p. 356
Sutcliffe, L. H. p. 281
Sutin, N. p. 378
Suttle, J. F. p. 336
Tate, J. F. p. 241
Taube, M. p. 174
Toth, K. S. p. 236
Wain, A. G. pp. 154, 346
Wahl, A. C. p. 201
Warren, C. G. p. 336
Weber, J. R. p. 281
Wendlandt, W. W. p. 276
White, J. C. p. 315
White, J. M. p. 122
Wilson, A. S. p. 327
Wolfsberg, K. p. 201
Woodhead, J. L. p. 154
Zingaro, R. A. p. 315

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 1 to 5. Pergamon Press Ltd. Printed in Great Britain.

# HALF-LIFE AND DECAY OF NIOBIUM-94*

R. P. SCHUMAN and P. GORIS

Phillips Petroleum Company, Atomic Energy Division, Idaho Falls, Idaho

(*Received* 23 *February* 1959; *in revised form* 31 *March* 1959)

**Abstract**—The specific activity of $^{94}$Nb has been determined by counting and mass-analysing two samples of reactor-irradiated niobium. The $\beta$-half-life of $^{94}$Nb is $(2{\cdot}03 \pm 0{\cdot}16) \times 10^4$ years. $^{94}$Nb emits $703 \pm 5$ keV and $874 \pm 5$ keV $\gamma$-rays with 100 per cent abundance; the 1580 keV crossover $\gamma$-ray has an abundance of $< 0{\cdot}05$ per cent. The $K$ electron capture branching of $^{94}$Nb is $< 6$ per cent of the $\beta$-decay. The $\gamma$-spectrum of 6·6 min $^{94m}$Nb has also been studied.

THE long-lived ground state of $^{94}$Nb, which is produced in neutron irradiated niobium, has been observed previously[1-3] These previous investigators obtained the half-life from the activity of $^{94}$Nb, the integrated flux (nvt), of the irradiation, and an absorption cross-section of $1{\cdot}1 \pm 0{\cdot}1$ barns for $^{93}$Nb.[4]

This laboratory has two samples of niobium which have received a much greater integrated flux than the samples previously studied, and which contain a sufficient percentage of $^{94}$Nb for accurate mass spectrometric analysis. These samples have been mass-analysed and counted, and a more precise half-life has been determined for $^{94}$Nb. The energies and abundancies of the $^{94}$Nb $\gamma$-rays have been redetermined.

The samples of spectroscopically pure niobium metal were irradiated in the Materials Testing Reactor to a total nvt of $\sim 6 \times 10^{21}$ and $\sim 12 \times 10^{21}$ neutrons/cm$^2$ respectively. The irradiation of the samples ended three years prior to the specific activity determinations, allowing 35 day $^{95}$Nb (due to second order capture) and 112 day $^{182}$Ta (from the activation of tantalum impurity) to decay essentially to zero activity. Even without further purification, the samples were radiochemically pure $^{94}$Nb plus $^{93m}$Nb.

The niobium was mass-analysed with a 60° single focusing mass spectrometer having a surface ionization source.[5] The ion source consisted of 50 to 100 $\mu$g of the irradiated metal powder on a heated tantalum filament; the beam was analysed for $Nb^+$ ions. Three mass peaks were found for the irradiated samples: the largest peak at mass 93 due to stable niobium, a small peak at mass 94 due to $^{94}$Nb, and a very small peak at mass 95 due to $^{95}$Mo produced by the decay of $^{95}$Nb second order capture product; no other molybdenum peaks were observed. The mass-analysis of unirradiated niobium showed only the mass 93 peak. Chemical analysis showed the presence of about 0·01 per cent of molybdenum in the most highly irradiated niobium.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

(1) D. L. DOUGLAS, A. C. MEWHERTER and R. P. SCHUMAN, *Phys. Rev.* **92**, 369 (1953).
(2) M. A. ROLLIER and E. SAELAND, *Phys. Rev.* **94**, 1079 (1954).
(3) M. A. ROLLIER, E. SAELAND, A. MORPUGO and A. CAGLIERIS, *Acta Chem. Scand.* **9**, 57 (1955)
(4) D. J. HUGHES *et al.*, U.S.A.E.C. Report AECU-2040 (1952).
(5) M. W. ECHO and T. D. MORGAN, *Analyt. Chem.* **29**, 1593 (1957).

The irradiated niobium samples contain $^{94}$Nb produced by neutron capture, and also $^{93m}$Nb, produced by the inelastic scattering of fast neutrons.[6] The $^{94}$Nb decays by the emission of a 0·50 MeV $\beta$-ray and 703 keV and 874 keV $\gamma$-rays in cascade.[1–3] The $^{93m}$Nb decays by the emission of conversion electrons and niobium X-rays from a 30·4 keV level.[7] The presence of $^{93m}$Nb precludes the use of $4\pi$ counting for the determination of the specific activity of $^{94}$Nb; consequently, the specific activity was determined by absolute $\gamma$-counting and by end-window $\beta$-counting through sufficient absorber to eliminate $^{93m}$Nb radiations.

The $\gamma$-counts were made with a 3 in. $\times$ 3 in. NaI(Tl) crystal and either a 20 channel or a 256 channel pulse-height analyser. The scintillation spectrometers had typical resolutions (full width at half-maximum) of 8·3 per cent for the 703 keV $\gamma$-ray and 7·8 per cent for the 874 keV $\gamma$-ray. The samples were placed 10·0 cm from

TABLE 1.—ACTIVITY OF A THIN $^{94}$Nb SAMPLE

| Type of ray | Absolute emission rate |
|---|---|
| 0·50 MeV $\beta$-ray | $2{\cdot}42 \times 10^5$ $\beta^-$/min |
| 874 keV $\gamma$-ray | $2{\cdot}37 \times 10^5$ $\gamma$/min |
| 703 keV $\gamma$-ray | $2{\cdot}42 \times 10^5$ $\gamma$/min |

the crystal, a plastic absorber interposed to stop $\beta$-rays, and the counting rate of each photopeak determined. The absolute $\gamma$-emission rates were calculated from the photopeak counting rate, the experimental peak to total ratios, the calculated counting efficiencies, and the $\gamma$-absorption in the plastic absorber.[8] It has been shown[8] that the $\gamma$-emission rates obtained in this manner are accurate to better than $\pm$ 5 per cent. As a check, the 662 keV $\gamma$-emission rate of a $\pm$ 5 per cent $^{137}$Cs source, the strength of which had been calibrated against a Bureau of Standards $^{137}$Cs standard, was determined by the above method and agreed within three per cent of the reported value.

The niobium $\beta$-counting rate determinations were made with a thin-window proportional counter, and the rates were compared with a $^{137}$Cs source which had been calibrated by $\gamma$-counting. The niobium samples for $\beta$-counting were very thin $Nb_2O_5$, mounted and counted in the same way as the $^{137}$Cs standard.

The abundances of the $^{94}$Nb $\beta$-ray and $\gamma$-rays were also redetermined. The $\gamma$-scintillation spectrum of $^{94}$Nb was measured with the sample at various distances from the crystal. A 1580 keV peak was observed which disappeared at large distances, indicating an abundance of less than 0·05 per cent for the crossover $\gamma$-ray; the 1580 keV peak observed at short distances was therefore a coincidence sum peak. Aluminium absorption measurements on the niobium $\beta$-rays did not show any $\beta$-ray of energy greater than 0·50 MeV (detection limit 2 per cent of the 0·50 MeV $\beta^-$). The absolute $\gamma$-emission rates, determined by scintillation counting agreed within experimental error with the $\beta$-disintegration rates, determined with an end-window proportional counter calibrated with a $^{137}$Cs standard (see Table 1). $\beta$-scintillation spectra

[6] R. P. SCHUMAN, *Phys. Rev.* **96**, 121 (1954).
[7] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).
[8] R. L. HEATH, U.S.A.E.C. Report IDO-16408 (1957).

Vol 12 1959/

of $^{94}$Nb showed no detectable conversion electrons, ($e/\gamma < 0{\cdot}02$), from the 703 and 874 keV $\gamma$-rays. The 874 keV $\gamma$-ray, which is also observed in $^{94}$Tc decay, is reported[9] to have a conversion coefficient of $10^{-3}$. It thus appears that the $\beta$-decay

TABLE 2.—DETERMINATION OF SPECIFIC ACTIVITY OF NIOBIUM SAMPLES

| Irradiation, nvt (neutrons/cm$^2$) | Counting sample | 703 keV ($\gamma$/sec, mg) | 874 keV ($\gamma$/sec, mg) |
|---|---|---|---|
| $\sim 6 \times 10^{21}$ | A | 58,300 | 57,040 |
| | B | 58,610 | 57,200 |
| | C | 58,410 | 56,900 |
| | Average | 58,440 ± 140 | 57,050 ± 130 |
| | | 57,750 ± 700 | |
| $\sim 12 \times 10^{21}$ | A | 110,100 | 106,000 |
| | A* | 107,800 | 106,400 |
| | B | 110,300 | 106,800 |
| | B* | 109,800 | 107,600 |
| | C | 110,900 | 108,800 |
| | C* | 110,900 | 109,200 |
| | Average | 110,000 ± 1,100 | 107,500 ± 1,200 |
| | | 108,700 ± 1,700 | |

* Measured with another spectrometer.

TABLE 3.—HALF-LIFE OF $^{94}$Nb

| Sample nvt (neutrons/cm$^2$) | Abundance of $^{94}$Nb (%) | Average $^{94}$Nb disintegration rate (disintegration/sec, mg Nb) | $^{94}$Nb half-life (years) |
|---|---|---|---|
| $\sim 6 \times 10^{21}$ | 0·813 ± 0·06 | 57,750 ± 700 | $2{\cdot}00 \times 10^4$ |
| $\sim 12 \times 10^{21}$ | 1·52 ± 0·07 | 108,700 ± 1,700 | $1{\cdot}99 \times 10^4$ |
| | 1·604 ± 0·11 | | $2{\cdot}10 \times 10^4$ |
| Average | | | $2{\cdot}03 \times 10^4$ |

of $^{94}$Nb proceeds by the emission of 0·50 MeV $\beta$-rays followed by essential unconverted 703 keV and 874 keV $\gamma$-rays in cascade. Thus the emission rate of each of the two $\gamma$-rays is the same (within 2 per cent) as the $\beta$-disintegration rate. The specific $\gamma$-activities for the half-life determinations were measured on weighed samples of niobium metal; these samples were somewhat thick for accurate end-window $\beta$-counting. The results and standard deviations of the specific activity measurements are summarized in Table 2. The mass analysis results and the calculated half-life are given in Table 3. The half-life of $^{94}$Nb for $\beta$-decay is $(2{\cdot}03 \pm 0{\cdot}16) \times 10^4$ years.

[9] H. MEDICUS, P. PREISWERK and P. SCHERRER, *Helv. Phys. Acta* **23**, 299 (1950).

The energies of the $^{94}$Nb $\gamma$-rays have been redetermined by comparison with the 511·0 keV annihilation radiation, the 661·6 keV $^{137}$Cs $\gamma$-ray, the 569·7 keV, 1064 keV and 1771 keV $^{207}$Bi $\gamma$-rays, and the 1172·8 keV and 1332.5 keV $^{60}$Co $\gamma$-rays.[7] The $^{94}$Nb $\gamma$-ray energies are 703 $\pm$ 5 keV and 874 $\pm$ 5 keV.

The mass difference, $^{94}$Zr–$^{94}$Mo, given in the literature, is equivalent to 1·14 $\pm$ 0·20 MeV.[10] Therefore, the electron-capture decay of $^{94}$Nb is energetically possible with an estimated decay energy of 0·9 $\pm$ 0·3 MeV. Since the level spacings of the even-even nuclides in the region of $^{94}$Zr are large,[7] it is expected that the electron capture decay of $^{94}$Nb will be energetically possible only to the ground state and possibly the first excited state (most likely 2+) of $^{94}$Zr. Thus, on the basis of the highly forbidden $\beta$-decay to the ground state and the 2+ state of $^{94}$Mo, it is expected that electron capture to $^{94}$Zr will be highly forbidden, and so the electron capture branching of $^{94}$Nb will be very small ($\ll$ 1 per cent of the $\beta$-decay).

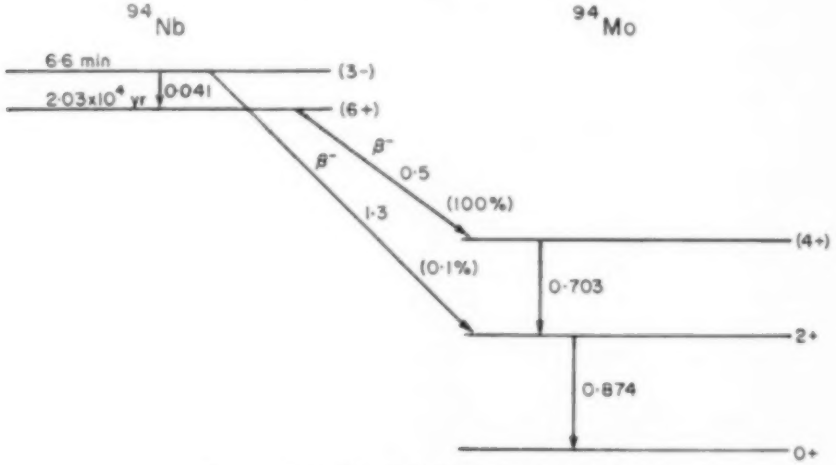



FIG. 1.—Decay scheme of $^{94}$Nb, energies in MeV.

The $K$ X-ray spectra of the niobium samples have been determined using a NaI(Tl) crystal with a beryllium window; no attempt was made to look for $L$ X-rays. The spectrometer had a resolution, full width at half-maximum, of about 33 per cent for the niobium X-rays. The spectra are indistinguishable from the niobium $K$ X-ray spectra of $^{93}$Mo, decaying by electron capture, and $^{94m}$Nb, decaying by isomeric transition. Comparison of Sr X-ray spectra with Nb X-ray spectra shows that the spectrometer should distinguish between Zr X-rays and Nb X-rays. Since the X-ray emission rate of the $Nb_2O_5$ sample is 30 per cent of the $\beta$-disintegration rate of $^{94}$Nb, and the X-rays are mainly niobium X-rays from $^{93m}$Nb, the $K$-electron capture branching of $^{94}$Nb cannot be more than a small fraction of 30 per cent of the $\beta$-decay. The $K$ capture branching is probably less than 6 per cent of the $\beta$-decay.

In order to obtain a more complete picture of the decay of $^{94}$Nb, the scintillation spectrum of 6·6 min $^{94m}$Nb has been studied. The spectrum showed intense niobium $K$ X-rays, a low intensity 41 $\pm$ 3 keV $\gamma$-ray and a 874 $\pm$ 10 keV $\gamma$-ray; no attempt was

[10] J. S. GEIGER, B. G. HOGG, H. E. DUCKWORTH and J. W. DEWDNEY, *Phys. Rev.* **89**, 621 (1953).

made to look for $L$ X-rays. In order to see if there is $\beta$-decay to the 1577 keV level in $^{94}$Mo, we have looked for the 703 keV $\gamma$-ray. No photopeak could be seen at this energy; however, the peak-to-valley ratio of the 874 keV $\gamma$-ray is not quite as large as would be expected, indicating a possibility of a 703 keV $\gamma$-ray with an abundance of $2 \pm 2$ per cent of the 874 keV $\gamma$-ray. The $K$ shell conversion coefficient of the 41 keV $\gamma$-ray, as determined from the $K$ X-ray to 41 keV $\gamma$-ratio, is $K/\gamma \sim 400$.

A suggested decay scheme of $^{94}$Nb is given in Fig. 1. The spins and parities are those proposed by KING.[11] A literature assignment of the isometric transition of 6·6 min $^{94m}$Nb is E3,[12] which is consistent with the level assignments. The 6·6 min $^{94m}$Nb $\beta$-transition to the 874 keV $^{94}$Mo level is first forbidden, $\log ft = 7{\cdot}3$, which is consistent with $\Delta I = 1$, yes. If the $\beta$-transition to the 1577 keV $^{94}$Mo level is about 2 per cent as abundant as the major beta, it will have $\log ft = 7{\cdot}5$ and so will be first forbidden and consistent with $\Delta I = 1$, yes. An assignment of $3+$ to the 1577 keV $^{94}$Mo level and $5+$ and $2-$ respectively to the $^{94}$Nb levels could also explain the observed niobium decay; however, these assignments appear less probable on the basis of $^{94}$Tc decay.[9,11]

*Acknowledgements*—The authors wish to express their appreciation to Mr. C. H. HOGG and Mr. R. L. HEATH for the use of the scintillation spectrometers and $\beta$-counter, and to the MTR reactor operators for the irradiations.

[11] R. W. KING, *Rev. Mod. Phys.* **26**, 350 (1954).
[12] M. GOLDHABER and A. W. SUNYAR, *Phys. Rev.* **83**, 906 (1951)

Vol. 12 59/60

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 6 to 7. Pergamon Press Ltd. Printed in Great Britain.

# HALF-LIVES OF $^{204}$Tl, RaD AND $^{207}$Bi*

G. HARBOTTLE
Chemistry Department, Brookhaven National Laboratory, Upton, L.I., New York

(*Received* 13 *April* 1959)

**Abstract**—Counting and balanced ion chamber measurements have given half-lives as follows: $^{204}$Tl 3·91 ± 0·07 years, RaD 20·4 ± 0·3 years, and $^{207}$Bi 30·2 ± 0·5 years.

*Thallium*-204

VARIOUS measurements of the half-life of this long-lived thallium isotope have been recently summarized.[1] In 1953 the author completed a series of measurements on a sample of thallium-204 which had been prepared by neutron irradiation, cooled for 2·2 years, carefully purified and counted in a "Nucleometer" (windowless, methane flow proportional counter) monthly for a period of about 2·9 years. A least-squares fit of the logarithm of counting rate vs. time yielded a half-life of 4·02 years.[2] A least-squares fit of the logarithm of the ratio of thallium counting rate to counting rate of a $U_3O_8$ standard over the same period gave 3·93 years.

Recently the sample of thallium was recounted in the same "Nucleometer". The intercept value of the least-squares fit of the earlier series of data was combined with the present counting rate to yield a half-life of 3·84 years over a decay interval of 8·88 years.

During the period 1954–55 the author prepared a new sample of $^{204}$Tl through irradiation of spectroscopic grade thallium metal with neutrons. This thallium was taken through many cycles of purification including scavenging with ferric hydroxide, oxidation–reduction, precipitation as thallous chromate and bromide and solvent extraction as thallic bromide. Two samples of this material differing in activity by a factor of two were taken: their half-lives were determined by use of a pair of balanced ion chambers. One sample was balanced against a source of radium and the other against a carefully-purified source of $^{99}$Tc. The decay of one thallium sample was followed for 160 days, the other for 120 days. A least-squares fit of the results yielded half-lives of 3·85 and 3·89 years respectively.

An average of the five above determinations, giving equal weight to each, gives the result $t_{\frac{1}{2}} = 3{\cdot}91 \pm 0{\cdot}07$ years. The consistency of all results, including those taken over shorter and longer times after irradiation, strongly argues that there is one and only one lifetime of the order of a few years, in neutron-irradiated thallium.

* Research performed under the auspices of the U.S. Atomic Energy Commission.

(1) J. E. EDWARDS, *J. Inorg. Nucl. Chem.* **7**, 336 (1958); R. W. FINK and B. L. ROBINSON, *Nucl. Phys.* **10**, 82 (1959).

(2) G. HARBOTTLE, *Phys. Rev.* **91**, 1234 (1953).



Vol 12 1959/

*Radium-D* (*lead*-210)

A supply of radium-D was obtained from spent radon needles and was purified by passage through a Dowex A-1 resin column in 2 M HCl. The material was finally converted to lead chromate. Radium-E ($^{210}$Bi) was allowed to grow into equilibrium with the radium-D. Radium-F ($^{210}$Po) was not in equilibrium, but its $\alpha$-rays were absorbed without being counted.

The radium-D, E equilibrium mixture was balanced against a $^{99}$Tc source and its decay followed over a period of 280 days in the balanced ion chambers. A least-squares fit of the data gave a half-life of 20·4 $\pm$ 0·3 years, in good agreement with literature values of 19·4[3] and 22[4] years.

*Bismuth*-207

The preparation and nuclear decay properties of this isotope have been described in a paper by ALBURGER and SUNYAR.[5] A portion of their material was balanced against a radium source and its decay followed in the balanced ion chambers over a period of 280 days. A least-squares fit of the data gave a half-life of 30·2 $\pm$ 0·5 years. This figure supersedes the value 27 $\pm$ 3 years of ALBURGER and SUNYAR which was based on the first portion of the measurements here reported.

This half-life is in good agreement with a recent value of 28 $\pm$ 3 years reported by SOSNIAK and BELL.[6] Their figure was an average of three determinations (based on a genetic method) which gave 24·3, 29·7 and 29·2 years. It is perhaps significant that two of their values are in very close agreement with that reported here. The half-life originally reported by NEUMANN and PERLMAN[7] was (approximately) 50 years while a much shorter half-life, 8·0 $\pm$ 0·6 years has been published by CHENG *et al.*[8] It is difficult to understand the large discrepancy between this and the 28- to 30-year figures mentioned above.

Vol.
12
59/60

*Acknowledgement*—The author is deeply indebted to Dr. S. KATCOFF of this laboratory for instruction, help and discussion of problems in the use of the balanced ion chambers.

[3] J. TOBAILEM, *J. Phys. Radium* **16**, 235 (1955).
[4] M. CURIE *et al.*, *Rev. Mod. Phys.* **3**, 427 (1931).
[5] D. E. ALBURGER and A. W. SUNYAR, *Phys. Rev.* **99**, 695 (1955).
[6] J. SOSNIAK and R. E. BELL, *Canad. J. Phys.* **37**, 1 (1959).
[7] H. M. NEUMANN and I. PERLMAN, *Phys. Rev.* **81**, 958 (1951).
[8] L. S. CHENG, V. C. RIDOLFO, M. L. POOL and D. N. KUNDU, *Phys. Rev.* **98**, 231A (1955).

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 8 to 11. Pergamon Press Ltd. Printed in Great Britain.

# ELECTRON-CAPTURE/NEGATRON-EMISSION BRANCHING RATIO OF $^{236}$Np (22 hr)*

J. E. GINDLER and R. K. SJOBLOM
Argonne National Laboratory, Lemont, Illinois

(*Received* 26 *March* 1959)

**Abstract**—A value of 1·05 ± 0·17 has been determined for the electron-capture/negatron-emission branching ratio of 22 hr $^{236}$Np using a combination of α-counting techniques and mass spectrometric measurements. The relative production of 22 hr $^{236}$Np to that of long-lived $^{236}$Np has been recalculated and found to be about seven for the interaction of 18 MeV deuterons with $^{235}$U.

THE amount of $^{236}$Np (22 hr) formed in a nuclear reaction is generally determined from the amount of $^{236}$Pu formed by the β-decay of the parent nucleus. By application of the electron-capture/negatron-emission branching ratio to the latter quantity the $^{236}$Np yield is determined. The value of the above branching ratio was first reported by ORTH and O'KELLEY[1] to be around two. Later work by PASSELL,[2] JAFFE[3] and GRAY[4] indicated the $K$ electron-capture/negatron-emission branching ratio as (43 ± 5 per cent)/(57 ± 5 per cent) with a lower limit for the $K/L$-capture ratio around four.[4]

The above values of the branching ratio were determined from electron, X-ray and γ-ray spectra measurements associated with the decay of $^{236}$Np and from α-activity measurements of the daughter nuclide, $^{236}$Pu. The present experiment was designed to measure directly the yields of both $^{236}$Np daughters by means of α-pulse analysis and mass spectrometric analysis.

## EXPERIMENTAL PROCEDURE

$^{236}$Np was prepared by the bombardment of a 0·020 in. thick metallic target of enriched uranium (93·3% $^{235}$U) with 20·7 MeV deuterons for a total of 1614 μA hr. The neptunium produced was isolated chemically within the 24 hr period immediately following the bombardment. A reduction by a factor greater than $10^7$ in the amount of uranium remaining with the neptunium was achieved by the following method. The uranium target was dissolved in hot nitric acid. The solution was diluted and the neptunium and plutonium present were carried on a $LaF_3$ precipitate. The precipitate was converted to the hydroxide, dissolved in 12 M HCl and placed on a Dowex A-1 anion resin column. Plutonium was eluted with 12 M HCl saturated with $NH_4I$. Neptunium and any residual plutonium and uranium were eluted with 1 M HCl. This fraction was made 12 M in HCl and 0·1 M in hydroquinone. The neptunium and any uranium reduced to the IV-state were extracted into a ten per cent solution of mono-octylphosphate in toluene.[5] After repeated scrubbing, the extracted elements were re-extracted into a 4 M HF–0·5 M HCl solution.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) D. A. ORTH and G. D. O'KELLEY, *Phys. Rev.* **82**, 758 (1951).
(2) T. O. PASSELL, University of California Radiation Laboratory Report UCRL-2528 (1954). Unpublished.
(3) H. JAFFE, University of California Radiation Laboratory Report UCRL-2537 (1954). Unpublished.
(4) P. R. GRAY, *Phys. Rev.* **101**, 1306 (1956).
(5) D. F. PEPPARD, G. W. MASON and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* **10**, 117 (1959).



Vol
12
1959/

The neptunium fraction was again subjected to the same chemistry described above—from the $LaF_3$ co-precipitation through the elution from the anion exchange column. The neptunium was then reduced to the IV-state and extracted into a 0·2 M thenoyltrifluoroacetone-benzene solution from which it was re-extracted into a 6 M HCl solution. The latter step was repeated once again.

The neptunium was allowed to decay several months after which $^{232}U$ was added to the solution as a chemical tracer. An aliquot of this solution was evaporated on to a platinum disk for α-pulse analysis. The result of this analysis is given in Table 1. The remainder of the solution was evaporated and the uranium separated from plutonium and neptunium in the following manner.

TABLE 1.—α-PULSE ANALYSIS OF DECAYED $^{236}Np$ (22 hr) SAMPLE WITH $^{232}U$ TRACER ADDED

| Nuclide | $^{236}Pu$ | $^{238}Pu$ | $^{232}U$ | $^{233, 234}U$ and $^{237}Np$ |
|---|---|---|---|---|
| Activity (%) | 85·60 ± 0·16 | 4·33 ± 0·10 | 9·62 ± 0·12 | 0·45 ± 0·04 |

The evaporated sample was taken up in 12 M HCl containing a small amount of nitric acid and placed on a Dowex A-1 anion resin column. The column was washed with 12 M HCl and plutonium eluted with 12 M HCl–$NH_4I$ solution. The column was further washed with an 80% 12 M HCl–20% 16 M $HNO_3$ solution followed by elution of the uranium with 12 M $HNO_3$. The column was then washed with 12 M HCl and the neptunium finally eluted with 0·5 M HCl. A $LaF_3$ precipitation was performed on the uranium fraction and the supernatant containing the uranium was evaporated to remove the fluoride ion. After several evaporations the uranium was dissolved in a ferrous solution saturated with $NH_4NO_3$ and extracted with diethyl ether.

Vol. 12 59/60

TABLE 2.—MASS SPECTROMETRIC ANALYSES OF URANIUM SAMPLES

| Sample | Nuclide composition in mole per cent | | | | | |
|---|---|---|---|---|---|---|
| | $^{232}U$ | $^{233}U$ | $^{234}U$ | $^{235}U$ | $^{236}U$ | $^{238}U$ |
| Target material | — | — | 0·910 ± 0·009 | 93·29 ± 0·05 | 0·432 ± 0·004 | 5·36 ± 0·05 |
| $^{232}U$ tracer | 2·70 ± 0·03 | 96·28 ± 0·04 | 0·839 ± 0·019 | 0·0142 ± 0·0011 | < 0·0006 | 0·164 ± 0·003 |
| Separated uranium | 0·0952 ± 0·004 | 3·24 ± 0·12 | 1·31 ± 0·05 | 89·76 ± 0·14 | 0·458 ± 0·005 | 5·13 ± 0·05 |

A portion of the separated uranium was submitted for mass spectrometric analysis, the result of which is shown in Table 2. Samples of the original target material and uranium tracer solutions were also purified by diethyl ether extraction and submitted for mass spectrometric analyses. These results are also shown in Table 2.

## RESULTS AND DISCUSSION

The electron-capture/negatron-emission (EC/$\beta^-$) branching ratio can be calculated from the data listed in Tables 1 and 2. The number of atoms of $^{236}Pu$, $N_{46}$, formed from the decay of $^{236}Np$ may be written as

$$N_{46} = \frac{A_T}{G_{46}} \frac{\tau_{46}}{\ln 2} \frac{D_{46}}{F} P_{46} \qquad (1)$$

where $P_{46}$ is the fraction of the α-activity attributed to $^{236}Pu$, $A_T$ the total activity of the sample in terms of counts per minute, $G_{46}$ the efficiency of the α-counter for $^{236}Pu$ α-particles, $\tau_{46}$ the $^{236}Pu$ half-life, $D_{46}$ is a correction for the growth and decay of

$^{236}$Pu from the time of chemical separation of the neptunium from the target material until the time of the pulse analysis, and $F$ is the fraction of total sample used for pulse analysis.

Similarly the number of $^{232}$U atoms, $N_{22}$, may be calculated from the relation

$$N_{22} = \frac{A_T}{G_{22}} \frac{\tau_{22}}{\ln 2} \frac{1}{F} P_{22} \tag{2}$$

$D_{22}$ is one for all practical purposes and is therefore omitted.

The atoms of $^{236}$U are then

$$N_{26} = N_{22} \frac{M_{26} - M'_{26}}{M_{22}} D_{26} \tag{3}$$

where $M_{26}$ is the total mole per cent $^{236}$U in the separated uranium sample, $M'_{26}$ is the mole per cent $^{236}$U in the separated uranium due to incomplete separation of the original target material and $M_{22}$ is the mole per cent $^{232}$U in the separated sample.

By combining the above three equations and making the assumption that $G_{22} = G_{46}$ then the electron-capture/negatron-emission branching ratio becomes

$$\frac{N_{26}}{N_{46}} = \frac{P_{22}\tau_{22}}{P_{46}\tau_{46}} \frac{M_{26} - M'_{26}}{M_{22}} \frac{D_{26}}{D_{16}} \tag{4}$$

$M'_{26}$ can be evaluated using the ratio $^{236}$U/$^{235}$U for the target material and the amount of $^{235}$U in the separated sample. This gives a value of $M_{26} - M'_{26}$ equal to 0·042. The value of $D_{26} = 1$ and $D_{46} = 0{\cdot}822$. Using values of 2·851 years[6] for $\tau_{46}$ and 73·6 years[7] for $\tau_{22}$, EC/$\beta^-$ is found to be 1·05 $\pm$ 0·17. More specifically, it is found that for every 100 disintegrations of 22 hr $^{236}$Np 51 $\pm$ 8 occur by electron capture and 49 $\pm$ 1 occur by negatron emission. The large error placed upon electron capture is primarily due to the subtraction of two large numbers $M_{26}$ and $M'_{26}$. It is felt that the difference between these two large values represents the growth of $^{236}$U from $^{236}$Np quite well. This confidence was gained by comparing the $^{238}$U/$^{235}$U ratio in the original with that in the separated sample. This showed agreement to within one per cent. Similarly, the $^{233}$U/$^{232}$U ratio in the tracer agreed with that in the separated sample within five per cent. The $^{234}$U/$^{235}$U ratio in the separated sample to that in the original is quite high even after the $^{234}$U added through tracer has been taken into account. The growth of $^{234}$U through the decay of $^{238}$Pu is insufficient to explain the discrepancy. However, the decay of $^{234}$Np which was formed during the deuteron bombardment readily accounts for this difference. This was shown by comparing the apparent increase of $^{234}$U with that of $^{236}$U in the following manner. The integrated cross-sections of the $^{235}$U ($d$, $3n$) $^{234}$Np and $^{235}$U ($d$, $n$) $^{236}$Np reactions were determined from the data of WING *et al.*[8] The ratio of these cross-sections was corrected for the decay of the respective nuclides during the deuteron bombardment and during the time from the end of the bombardment until the final chemical separation of neptunium from uranium. The EC/$\beta^-$ branching ratio of $^{236}$Np was applied to

[6] D. C. HOFFMAN, G. P. FORD and F. O. LAWERNCE, *J. Inorg. Nucl. Chem.* **4**, 143 (1957).
[7] P. A. SELLERS, C. M. STEVENS and M. H. STUDIER, *Phys. Rev.* **94**, 952 (1954).
[8] J. WING, W. J. RAMLER, A. L. HARKNESS and J. R. HUIZENGA, *Phys. Rev.* **114**, 163 (1959).

Vol 12 1959/

determine the apparent increase of $^{236}$U with respect to $^{234}$U. This value agreed to within ten per cent of the value found by use of the mass spectrometric data. The increase in the mass of $^{235}$U formed by the decay of $^{235}$Np was calculated to be less than one per cent of the value given in Table 2 for the separated sample.

The difference between the value of $1{\cdot}05 \pm 0{\cdot}17$ for the EC/$\beta^-$ branching ratio obtained in the present experiment and the value of 0·75 for the $K/\beta^-$ branching ratio obtained by others[2–4] may be assumed to be caused by $L$- and possibly higher order capture events. By use of the above values one can evaluate the contribution of capture events other than $K$-capture to the branching ratio. A simple calculation shows the $L + \ldots/\beta^-$ branching ratio to be $0{\cdot}30 \pm 0{\cdot}20$ and the $K/L + \ldots$ capture ratio to be $2{\cdot}5 \pm 1{\cdot}7$. (The authors have used a limit of $\pm 0{\cdot}11$ for the $K/\beta^-$ value.) GRAY[4] has placed a lower limit of around four on the $K/L$-capture ratio.

A long-lived isomer of $^{236}$Np has been found to exist.[9] Recent measurements[10] have indicated that the 18 MeV deuteron production of the 22 hr isomer to that of the long-lived isomer in $^{235}$U is six. This value assumes that a negligible amount of the long-lived isomer is made by isomeric transition but is produced directly. A recalculation of this value using the EC/$\beta^-$ branching ratio presented herein indicates that the production of 22 hr $^{236}$Np to that of long-lived $^{236}$Np is approximately seven.

*Acknowledgements*—We wish to acknowledge the assistance of W. RAMLER, A. SCHULKE and members of the Argonne 60 in. cyclotron group for making possible the deuteron bombardment. Special thanks are due to L. HARKNESS and D. HENDERSON for the mass spectrometric analyses and $\alpha$-pulse analyses, respectively.

Vol. 12 59/60

[9] M. H. STUDIER, J. E. GINDLER and C. M. STEVENS, *Phys. Rev.* **97**, 88 (1955).
[10] J. E. GINDLER, J. R. HUIZENGA and D. W. ENGELKEMEIR, *Phys. Rev.* **109**, 1263 (1958).

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 12 to 17. Pergamon Press Ltd. Printed in Great Britain.

# NATURAL OCCURRENCE OF THE SHORT-LIVED BARIUM AND STRONTIUM ISOTOPES*†

H. R. HEYDEGGER‡ and P. K. KURODA
Department of Chemistry, University of Arkansas, Fayetteville, Arkansas

(*Received* 21 *December* 1958; *in revised form* 15 *April* 1959)

**Abstract**—The equilibrium ratio of $^{140}Ba$ to $^{238}U$ in non-irradiated uranium salts with both the natural isotopic ratio and a depletion in $^{235}U$ has been determined. The ratio, expressed in terms of $10^{-4}$ disintegrations per sec per g of $^{238}U$, is $6{\cdot}2 \pm 0{\cdot}7$. The results from natural and depleted uranium salts were found to agree within the experimental error. If SEGRÈ's value of the spontaneous fission half-life of $^{238}U$, $(8{\cdot}04 \pm 0{\cdot}3) \times 10^{15}$ years, is taken to be correct, the spontaneous fission yield of $^{140}Ba$ from $^{238}U$ is found to be $9{\cdot}6 \pm 1{\cdot}2$ per cent.

IT has recently been demonstrated by KURODA and EDWARDS[1,2] that $^{90}Sr$ and $^{140}Ba$ occur in pitchblende and in natural uranium salts, respectively. It appears that these nuclides are produced mostly by the $^{238}U$ spontaneous fission process in nature and, hence, their abundance in the earth's crust is not necessarily negligibly small as compared with the quantities of these nuclides produced artificially.[3]

LIBBY[4] estimated that the quantity of the artificially produced $^{90}Sr$ in the stratosphere in 1956 was approximately 10 m curie/mile$^2$ of the earth's surface. From the average abundance of uranium in igneous rocks (4 g per ton) and the equilibrium ratio of $^{90}Sr$ : $^{238}U$ in uranium bearing materials (approximately $1 \times 10^{-14}$ curie per g $^{238}U$[1]) the total quantity of $^{90}Sr$ in the earth's ten-mile crust is calculated to be approximately 5 m curie/mile$^2$ of the earth's surface.

It has been reported by FLEMING and THODE[5] and WETHERILL[6] that the thermal neutron-induced fission of $^{235}U$ occurs in some uranium minerals. It is difficult to estimate the contribution of thermal neutron-induced fission of $^{235}U$ in the production of the fission products in various uranium-bearing materials. ASHIZAWA and KURODA[7] and PARKER and KURODA[8] have recently reported that the equilibrium ratios of the short-lived iodine isotopes to $^{238}U$ and $^{99}Mo$ to $^{238}U$, respectively, in depleted uranium salt (99·989% $^{238}U$ and 0·011% $^{235}U$) are the same as the corresponding ratios in natural uranium salt.

* This paper represents a part of the dissertation submitted by H. R. HEYDEGGER to the graduate School of the University of Arkansas in partial fulfilment of the requirements for the degree of Master of Science.

† Presented at the 132nd National Meeting of the American Chemical Society, 11 September, 1957, New York.

‡ Present address: Enrico Fermi Institute for Nuclear Studies, University of Chicago, Chicago, Illinois.

(1) P. K. KURODA and R. R. EDWARDS, *J. Chem. Phys.* **22**, 1940 (1954).
(2) P. K. KURODA and R. R. EDWARDS, *J. Inorg. Nucl. Chem.* **3**, 345 (1957).
(3) P. K. KURODA, ANL-5920, Argonne National Laboratory (1958).
(4) W. F. LIBBY, *Proc. Nat. Acad. Sci. U.S.* **42**, 365 (1956).
(5) W. H. FLEMING and H. G. THODE, *Phys. Rev.* **92**, 378 (1953).
(6) G. W. WETHERILL, *Phys. Rev.* **92**, 907 (1953).
(7) F. T. ASHIZAWA and P. K. KURODA, *J. Inorg. Nucl. Chem.* **5**, 12 (1957).
(8) P. L. PARKER and P. K. KURODA, *J. Inorg. Nucl. Chem.* **5**, 153 (1958).



Vol. 12 1959/6

Measurements of the equilibrium ratios of $^{90}Sr/^{238}U$ and $^{140}Ba/^{238}U$ were made with pitchblende and with natural uranium salts in the previous works[1,2] and the ordinary end-window Geiger counters without anti-coincidence system were used for the radioactivity measurements.

The primary purpose of this study was to repeat the experiments with a more sensitive low-level counting equipment and with the depleted uranium salt. Because of the relatively long half-life of $^{90}Sr$, measurement of the $^{90}Sr/^{238}U$ equilibrium ratio in depleted uranium salt could not have been carried out. However, some attempt has been made, instead, to measure the quantities of $^{139}Ba$, $^{91}Sr$ and $^{92}Sr$ in non-irradiated natural and depleted uranium salts.

## EXPERIMENTAL

*Natural uranium solution*

A total of 900 g of commercial uranyl nitrate (Mallinckrodt Reagent grade) was dissolved in 4 l. of reagent grade ether and carefully purified by extraction of trace contaminations with an aqueous barium nitrate solution. The isotopic composition was assumed to be 99·276% $^{238}U$ and 0·719% $^{235}U$.

*Depleted uranium solution*

A total of 2000 g of depleted uranium as the oxide was dissolved in about 6 l. of 3 N nitric acid and exhaustively purified. The solution was finally evaporated to dryness, dissolved in ether and purified as above. The isotopic composition was 99·989% $^{238}U$ and 0·011% $^{235}U$, according to Dr. R. B. MARTIN of the United States Atomic Energy Commission, Oak Ridge, Tennessee.

*Other reagents*

All other reagents were commercial reagent grade and were repeatedly monitored for radiochemical purity. The control experiments showed the necessity for frequent preparation of new reagent solutions.

*Counting equipment*

A pancake-type Geiger–Müller counter (Anton 1007TA, 2 mg/cm$^{-2}$ mica window), which had a background of 1·10 ± 0·05 counts/min in anti-coincidence with the surrounding counters, was used for the radioactivity measurements. The counter was calibrated according to the method described by STEINBERG.[9]

Two 100λ portions of a stock solution, which contained approximately 500 μcuries of $^{140}Ba + ^{140}La$ equilibrium mixture per litre, were evaporated on thin Tygon films and counted in a 4π cylindrical counter, to obtain the exact concentration of the $^{140}Ba + ^{140}La$ equilibrium mixture in the stock solution. A series of fifteen $^{140}Ba + ^{140}La$ standards, each containing an identical quantity of $^{140}Ba + ^{140}La$, but with various carrier weights ranging from 0 to 300 mg, were prepared from the above stock solution and used for the calibration.

*Extraction and purification of the barium fraction*

The extraction of the barium fraction from the uranium solution was made by the addition of a small portion (about 10 ml) of aqueous barium nitrate solution (about 5 mg/ml) to about 700 ml of ethereal uranium solution in a separatory funnel. The funnel was shaken and the aqueous layer drawn off. Addition and removal of the aqueous solution was repeated and the aqueous layers combined and heated nearly to boiling. Sulphuric acid was added and the solution allowed to digest and cool to room temperature. The barium sulphate precipitate was collected by suction filtration on to a filter disk and converted to barium carbonate by fusion with anhydrous sodium carbonate. The remainder of the purification consisted of a series of ferric hydroxide scavenging steps and barium nitrate precipitation steps. The barium was finally precipitated as the carbonate or chromate, washed, dried, weighed and mounted on aluminium for radioactivity measurement.

[9] E. P. STEINBERG, ANL-5622, Argonne National Laboratory (1956).

*Control experiments*

Application of the procedure outlined above to a 10 g sample of uranyl nitrate resulted in a barium fraction which gave 0·00 ± 0·04 counts/min above background. Calculations showed that no detectable activity is to be expected from such a small uranium sample if the chemical procedure is effective.

A study of the distribution of carrier barium and $^{140}Ba$-$^{140}La$ activity between the aqueous and ethereal layers showed that the aqueous extraction method employed is very nearly 100 per cent effective.

A preliminary experiment using 258 g of $^{238}U$ was performed as outlined above. Purification consisted of five nitrate precipitation and eleven iron scavenging steps, with the barium being finally collected as the carbonate. The chemical yield of the carrier was about 25 per cent and the results were of the expected order, indicating that the chemical procedure, as developed, was applicable to large-scale determinations.

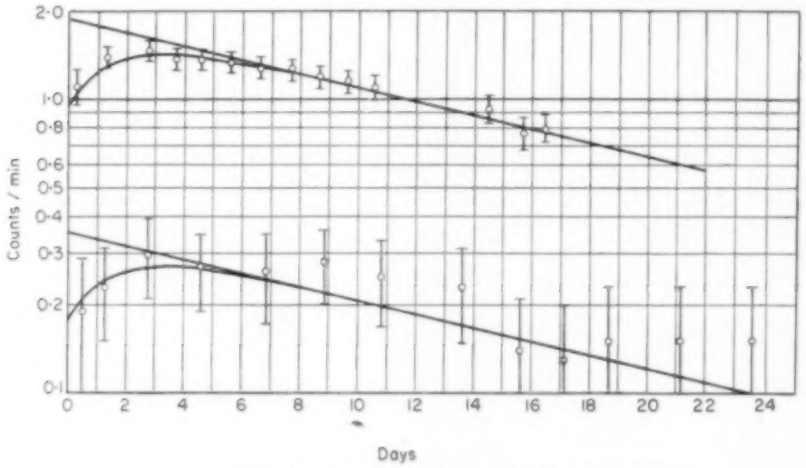



FIG. 1.—Activity of barium fraction from natural uranium salts.

## EXPERIMENTAL RESULTS AND DISCUSSION

A natural uranium solution containing 758 g of $^{238}U$ was treated as outlined above. Purification consisted of three nitrate precipitation and five iron scavenging steps. The barium was finally collected as the carbonate and the chemical yield found to be 35·4 per cent. The barium activity had been allowed to grow into the uranium solution for forty-nine days since the last previous barium extraction. The background was 1·10 ± 0·03 counts/min and a correction of 0·06 ± 0·03 counts/min was applied for residual contamination not removed by the purification process. The results of this experiment are shown as the upper curve in Fig. 1. The characteristic 40 hr growth of $^{140}La$ from $^{140}Ba$ until equilibrium is reached, and from that point, the 12·8 day decay of $^{140}Ba$ are displayed. The activity of $^{140}Ba$ at the time of separation of barium sulphate was calculated to be 0·94 ± 0·10 counts/min. This corresponds to 28·1 ± 3·0 disintegration/min using the value of 35·4 per cent for the chemical yield and 9·5 per cent for the overall detection efficiency. The counting data are presented in Table 1.

A natural uranium solution containing 401 g of $^{238}U$ was treated as outlined above. The purification consisted of six iron scavenging and three nitrate precipitation steps, with the barium being finally collected as the chromate. Recovery of the carrier

Vol. 12 1959/6

TABLE 1.—ACTIVITY OF THE BARIUM FRACTION FROM NATURAL URANIUM

| Time after initial Ba separation (min) | Observed activity (c.p.m.) | Observed activity less background (c.p.m.) | $^{140}$Ba plus $^{140}$La activity* (c.p.m.) |
|---|---|---|---|
| 0 | — | — | 0·94 ± 0·10† |
| 410 | 2·27 | 1·17 | 1·11 ± 0·15 |
| 1221 | 2·54 | 1·44 | 1·38 ± 0·09 |
| 2619 | 2·63 | 1·53 | 1·47 ± 0·11 |
| 3922 | 2·52 | 1·42 | 1·36 ± 0·11 |
| 5256 | 2·52 | 1·42 | 1·36 ± 0·10 |
| 6726 | 2·50 | 1·40 | 1·34 ± 0·10 |
| 8123 | 2·44 | 1·34 | 1·28 ± 0·10 |
| 9702 | 2·42 | 1·32 | 1·26 ± 0·10 |
| 11170 | 2·34 | 1·24 | 1·18 ± 0·10 |
| 12481 | 2·30 | 1·20 | 1·14 ± 0·10 |
| 13887 | 2·25 | 1·15 | 1·09 ± 0·10 |
| 20151 | 2·01 | 0·91 | 0·85 ± 0·10 |
| 21248 | 1·93 | 0·83 | 0·77 ± 0·10 |
| 23772 | 1·95 | 0·85 | 0·79 ± 0·10 |

* Corrected for 0·06 ± 0·03 counts/min of residual contamination.
† Calculated value.

was found to be 51·8 per cent. Five days had elapsed since the last previous barium extraction. The correction for residual contamination was 0·06 ± 0·03 counts/min and the background was 1·07 ± 0·03 counts/min. The lower curve in Fig. 1 presents the results of this experiment and displays the characteristic growth and decay of the barium fraction. The counting data are presented in Table 2. The activity of the $^{140}$Ba at the time of the sulphate separation was calculated to be 0·17 ± 0·03 counts/min.

TABLE 2.—ACTIVITY OF THE BARIUM FRACTION FROM NATURAL URANIUM

| Time after initial Ba separation (min) | Observed activity (c.p.m.) | Observed activity less background (c.p.m.) | $^{140}$Ba plus $^{140}$La activity* (c.p.m.) |
|---|---|---|---|
| 0 | — | — | 0·17 ± 0·03† |
| 744 | 1·32 | 0·25 | 0·19 ± 0·10 |
| 1820 | 1·36 | 0·29 | 0·23 ± 0·09 |
| 4060 | 1·43 | 0·36 | 0·30 ± 0·08 |
| 6659 | 1·40 | 0·33 | 0·27 ± 0·09 |
| 9897 | 1·39 | 0·32 | 0·26 ± 0·09 |
| 12810 | 1·41 | 0·34 | 0·28 ± 0·09 |
| 14980 | 1·38 | 0·31 | 0·25 ± 0·08 |
| 18276 | 1·35 | 0·28 | 0·22 ± 0·08 |
| 21870 | 1·26 | 0·19 | 0·13 ± 0·08 |
| 25482 | 1·28 | 0·21 | 0·15 ± 0·08 |
| 29046 | 1·28 | 0·21 | 0·15 ± 0·08 |
| 32661 | 1·28 | 0·21 | 0·15 ± 0·08 |

* Corrected for 0·06 ± 0·03 counts/min residual contamination.
† Calculated value.

This corresponds to $3{\cdot}7 \pm 0{\cdot}6$ disintegration/min using the value of 51·8 per cent for the chemical yield and 8·9 per cent for the overall detection efficiency.

The spontaneous fission yield, $y$, of $^{140}$Ba from $^{238}$U can be calculated on the basis of the data by the use of the following equation:

$$y = \frac{N_2\lambda_2}{N_1\lambda_1\{1 - \exp(-\lambda_2 t)\}}$$

where $N_2$ is the number of atoms of $^{140}$Ba, $\lambda_2$ is the decay constant of $^{140}$Ba, $N_1$ is the number of atoms of $^{238}$U, $\lambda_1$ is the decay constant of $^{238}$U for spontaneous fission, and $t$ is the time elapsed since the last previous extraction of barium from the uranium solution. For the calculation of $\lambda_1$, SEGRÈ's value of $(8{\cdot}04 \pm 0{\cdot}3) \times 10^{15}$ years[10]

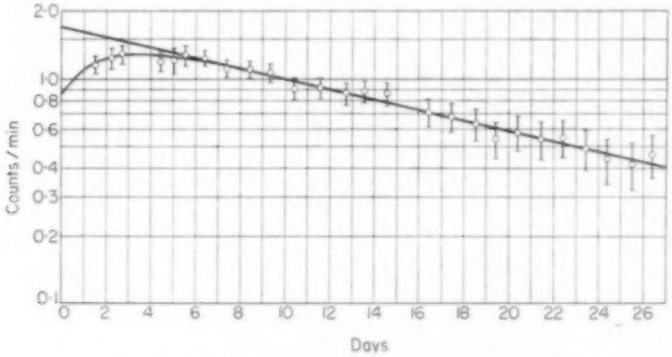



FIG. 2.—Activity of barium fraction from natural uranium salts.

was assumed for the spontaneous fission half-life of $^{238}$U. Values of $9{\cdot}60 \pm 1{\cdot}0$ and $9{\cdot}54 \pm 0{\cdot}5$ per cent, respectively, are obtained for $y$ from the two experiments with natural uranium.

It is interesting to note that the good agreement in the results of the two natural uranium experiments shows that the activity of the barium fraction does indeed grow into the uranium solution according to the predictions based upon the spontaneous fission-rate and would, therefore, seem to preclude the possiblity of contamination in the form of extra $^{140}$Ba or some other $\beta$-active species from some outside source. This is supported by the fact that control experiments run immediately prior to both natural uranium experiments showed $0{\cdot}00 \pm 0{\cdot}05$ counts/min of activity above background.

An ethereal depleted uranium solution containing 932 g of $^{238}$U was treated as outlined above. Purification consisted of three nitrate precipitation and eight iron scavenging steps. The barium was finally collected as the carbonate. Recovery of the carrier was 22·0 per cent. The barium activity had been allowed to grow into the uranium solution for 127 days since the last previous barium extraction and was assumed to be at equilibrium. The correction for residual contamination was $0{\cdot}15 \pm 0{\cdot}05$ counts/min. The background was $1{\cdot}15 \pm 0{\cdot}03$ counts/min. The results of the radioactivity measurements are shown in Fig. 2. The activity of $^{140}$Ba at the time

[10] E. SEGRÈ, *Phys. Rev.* **86**, 21 (1952).

Vol. 12 1959/6

of the sulphate separation was calculated to be $0.85 \pm 0{\cdot}10$ counts/min. This corresponds to $40{\cdot}6 \pm 5{\cdot}0$ disintegrations/min using the value of 22·0 per cent for the chemical yield and 9·5 per cent for the overall detection efficiency. The data from the depleted uranium experiment yield a value of $y = 10{\cdot}6 \pm 1{\cdot}2$ per cent, which is in agreement with the value for natural uranium, within the experimental error. The rather large fraction of residual contamination observed in the depleted uranium experiment remained unexplained. It is possible, however, that depleted uranium salt used in the experiment contained traces of radium isotopes which had not been completely removed during the purification procedure.

Similar difficulties were encountered during the course of investigation on the radioactive fallout by one of the authors.[3] When the $^{140}$Ba concentration in rain water was less than a few micromicrocuries per litre, a residual contamination of the order of magnitude of a few tenths counts/min was occasionally observed, and it has been tentatively attributed to the presence of radium in rain water. However, it is also possible that the radium contamination originated from reagents or dust particles. The problem is being further investigated in this laboratory.

A theoretical evaluation of the contribution from thermal neutron-induced fission has been made by the application of the principles of the nuclear chain-reaction to the experimental system. The details of such a calculation have been presented previously.[7] In the experimental system represented by the second uranium experiment, the value of the effective multiplication constant obtained indicated a contribution from thermal neutron-induced fission of $^{235}$U of much less than 1 per cent. It might be noted that the flux in the case of fast cosmic ray neutron-induced fission of $^{238}$U is so low near the earth's surface that considerably less than 0·01 counts/min is contributed in the experimental system. A similar result should also hold for cosmic ray meson-induced fission.

Some attempt has been made to modify the procedure described above to determine the yields of $^{139}$Ba, $^{91}$Sr and $^{92}$Sr. The presence of the above-mentioned nuclides in non-irradiated uranium salts was verified and the following tentative values for $y$ were obtained: $y(^{91}\text{Sr}) = 6 \pm 5$ per cent and $y(^{92}\text{Sr}) = 12 \pm 5$ per cent. The value of $y$ for $^{139}$Ba could not have been obtained since the chemical procedure required more than 2 half-lives of this nuclide. Further work on these problems is contemplated.

*Acknowledgements*—This investigation was made possible by support from the United States Atomic Energy Commission. The depleted uranium sample used in this study was kindly supplied to the authors by Dr. H. M. Roth of the Research and Development Division, United States Atomic Energy Commission, Oak Ridge, Tennessee.

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 18 to 29. Pergamon Press Ltd. Printed in Great Britain.

# REACTIONS OF NEUTRON-ACTIVATED ARSENIC ATOMS IN ORGANIC MEDIA—I

## FORMATION OF PHENYL ARSENIC COMPOUNDS DURING NEUTRON IRRADIATION OF ARSENIC TRICHLORIDE IN BENZENE

K. E. SIEKIERSKA, A. SOKOŁOWSKA and I. G. CAMPBELL

Department of Radiochemistry, Institute of Nuclear Research, Warsaw

(*Received* 16 *December* 1958; *in revised form* 16 *April* 1959)

**Abstract**—During the pile irradiation of arsenic trichloride in benzene, formation has been observed of diphenyl and monophenyl arsenic compounds. The intervention of billiard-ball type collisions is excluded in this case, and the result must be attributed to the formation of phenyl radicals by collisions of arsenic atoms of high kinetic energy with benzene molecules, or activation of benzene molecules during neutralization of the positive charge acquired by the arsenic atom as a result of the $(n, \gamma)$ reaction.

The result is compared with results of irradiation of triphenylarsine, in which both billiard-ball collisions and radical type mechanisms could play a part.

A paper chromatographic technique has been developed to supplement column chromatography for separating the products of irradiation.

Vol.
12
1959/6

CAREFUL studies of the products of neutron irradiation of triphenyl stibine[1] and triphenyl arsine,[2–4] have shown that alongside the antimony or arsenic activity remaining in the triphenyl compound or present as inorganic forms, a considerable proportion of the $^{122,124}Sb$ or $^{76}As$ atoms are found in diphenyl or monophenyl compounds.

*A priori* it is possible to conceive that both billiard-ball type collisions, of the type suggested by LIBBY,[5] or radical type mechanisms of the type postulated by WILLARD *et al.*,[6] could explain the retention of activity in the organic compounds in these systems. The very small fraction of activity retained in the triphenyl compound might represent that proportion of atoms which failed to rupture even one bond as a result of neutron activation. On the billiard-ball collision hypothesis, diphenyl or monophenyl compounds would be formed as a result of a transfer of energy from a collision between a naked hot arsenic atom and an inactive arsenic atom in triphenyl

(1) R. M. HALL and N. SUTIN, *J. Inorg. Nucl. Chem.* **2**, 185 (1956).
(2) A. G. MADDOCK and N. SUTIN, *Trans. Faraday Soc.* **184** (1955).
(3) F. LENZ and I. W. RUDERMAN, *Progr. Rep. Nucl. Phys.* Columbia Univ. C.U.D. **94**, 29 (March, 1951).
(4) F. LENZ and I. W. RUDERMAN, *Progr. Rep. Nucl. Phys.* Columbia Univ. C.U.D. **61**, 11 (September, 1950).
(5) W. F. LIBBY, *J. Amer. Chem. Soc.* **69**, 2523 (1947).
(6) J. E. WILLARD *et al.*, *Ann. Rev. Nucl. Sci.* **3**, 193 (1953).

arsine, whereby the latter is expelled completely from the molecule, and two or one of the three phenyl radicals formed about the site of collision combine with the cooled $^{76}As$ atom. The valencies of the $^{76}As$ not thus occupied by benzene rings, then combine with oxygen or hydrogen to form phenyl arsine, phenyl arsenic acids or phenyl arsine oxides. One might expect that a certain number of phenyl radicals would be dispersed after $^{76}As$, $^{75}As$ collisions, so that catching of all three radicals by a cooled $^{76}As$ atom after expulsion of the inactive As atom would be improbable and catching of two phenyl radicals would be a somewhat less probable process than catching one, which would accord with the distribution of activity found in the organic products.[2]

Formation of monophenyl and diphenyl compounds of arsenic could also be explained on the basis of the formation of phenyl radicals by inelastic collisions of recoiling $^{76}As$ atoms with the benzene rings of the irradiated triphenyl arsine, and subsequent combination of these radicals with $^{76}As$ atoms after the latter have become thermalized as a result of successive collisions. This mechanism has been proposed to explain in part the formation of monophenyl and diphenyl arsenic compounds by the authors of the most recent publication on the effects of neutron irradiation of triphenyl arsine and is supported by the finding that part of the formation of phenyl arsenic bonds takes place as a thermal reaction during and after irradiation.[2]

It must also be borne in mind that weaker $\gamma$-quanta emitted by compound nuclei after neutron capture can be extensively converted internally, and that in all cases so far studied the activated atom has been found to possess a positive charge resulting from an Auger shower after the conversion.[7] During discharge of any charge possessed by $^{76}As$ by electron transfer from molecules in the environment, some tens of electron volts of ionization energy may be released, and it may be expected that disintegration of triphenyl arsine molecules would result, accompanied by formation of phenyl radicals.

From the experiments previously described it is impossible to draw any conclusions as to the relative participation of billiard-ball or radical mechanisms in the formation of organic compounds by hot As atoms.

In general although experiments with halogen scavengers and other approaches prove that billiard-ball collisions do not explain a considerable proportion of the events leading to retention,[6] no direct evidence has been found which excludes the participation of such mechanisms in that fraction of events which is found to be insensitive to the presence of a radical scavenger. It has been pointed out elsewhere by one of the authors[8] in connexion with experiments on neutron irradiated tributyl phosphate, that systems involving polyvalent atoms may offer certain useful features in studying the relative roles of billiard-ball and radical mechanisms.

It has been decided to examine the mechanisms of formation of phenyl arsenic compounds from this point of view. The obvious approach, by analogy with work on the organic halides, is to study the irradiation of inorganic arsenic compounds in benzene where billiard-ball collisions leading to formation of organic compounds are excluded, and the results of such experiments are presented here.

[7] C. T. Hibdon and C. O. Muehlhause, *Phys. Rev.* **88**, 943 (1952).
[8] I. G. Campbell, A. Poczynajło and A. Suida, *J. Inorg. Nucl. Chem.* **10**, 255 (1959).

## EXPERIMENTAL

### *Materials*

Triphenylarsine (TPA), diphenylarsine oxide (DPO), phenylarsine oxide (PO), diphenylarsonic acid (DPA) phenylarsonic acid (PA) were prepared by appropriate methods.[9–13] DPO-$^{76}$As, PO-$^{76}$As and PA-$^{76}$As were also prepared from $^{76}AsO_3$. The inactive substances were all recrystallized several times to ensure high purity and had satisfactory melting points.

All inorganic carriers were analytical grade. Solvents were dried and redistilled before use, and in the case of the benzene and ethanol used for elution, were further purified by passage through a column of alumina.

$AsCl_3$ was purified immediately before encapsulating for irradiation by distillation through a Vigreux column, the 130·5–131°C fraction being used.

### *Irradiation*

Samples were irradiated in the thermal column of the JENER experimental reactor at Kjeller, Norway, at a thermal neutron flux of $10^8$neutrons/cm$^2$ per sec for approximately 3–4 $^{76}$As half-lives, and in the thermal column of the Polish reactor "EWA" at $10^9$neutrons/cm$^2$ per sec for 1–2 half-lives or $10^{12}$neutrons/cm$^2$ per sec for one half-life. Samples were enclosed in quartz or glass capsules for irradiation, at atmospheric pressure in the case of solutions, and *in vacuo* in the case of crystals. Samples were protected from light from the moment of packing until opening after irradiation. The following samples were irradiated:

(1) 0·1 M $AsCl_3$ in dry benzene
(2) Crystalline TPA
(3) 0·1 M TPA in dry benzene

Paper chromatograms were activated at $10^{12}$neutrons/cm$^2$ per sec in the thermal column of "EWA" for about 6 hr.

### *Chromatography*

Separation of reaction products was based on the procedure of MADDOCK and SUTIN, involving elution with a series of solvents from an alumina column.[2] It was found necessary to modify this method somewhat, and in particular to supplement it by paper chromatography.

Alumina was chromatographic grade.* Decantation was used to regulate grain size, followed by drying at 200°C for 10 hr. Methylene blue activity was $4{\cdot}2 \times 10^{-6}$ mole MB/g.[14] Columns were 0·6 cm diameter and 12 cm long. Columns were filled with a slurry of alumina in benzene and discarded after using once.

Solutions were passed through the column at 30–40 ml/hr under slight positive pressure from a bicycle pump, and collected in 2 or 5 ml lots in calibrated receptacles.

Paper chromatography was done on Whatman No. 1 paper, previously washed with 0·5 per cent sodium versenate solution, followed by repeated washing with distilled water and air drying.

The following methods were used to identify the fraction eluted or separated. The most general method was the distribution of $^{76}$As activity in fractions eluted from columns after addition of one marked compound in the presence of other inactive carriers. The fact that DPO gives no precipitate with $HgCl_2$ in ether solution whereas TPA precipitates, was used as additional identification in eluates containing these two compounds. Radioactivation analysis was used to identify and to estimate components separated by paper chromatography and to determine $R_f$ values in various solvent systems. For this purpose inactive carriers were chromatogrammed singly or in mixtures and after drying at 60°C the strips were activated in the reactor, afterwards scanning with an end-window G.M. tube with a 0·5 cm width slit in the mask.

* Alumina was from Gławchimreaktiv, U.S.S.R.

[9] P. PFEIFFER, *Ber. Dtsch. Chem. Ges.* **37**, 4621 (1904).
[10] J. BLICKE and H. SMITH, *J. Amer. Chem. Soc.* **51**, 1561 (1929).
[11] J. BLICKE and H. SMITH, *J. Amer. Chem. Soc.* **52**, 2947 (1930).
[12] W. DENN and L. WILCOX, *J. Amer. Chem. Soc.* **35**, 43 (1946).
[13] R. H. BULLARD and J. B. DICKEY, *Organic Syntheses* Vol. II, p. 494. Wiley, New York (1950).
[14] G. HESSE, I. DANIEL and G. WOHLLEBEN, *Angew. Chem.* **64**, 103 (1952).

Vol. 12 1959/6

First of all the distribution of $^{76}As$ added as labelled organic or inorganic compounds was determined in the presence of other non-labelled carriers by elution of the column with the series of solvents used by MADDOCK and SUTIN; arsines and $As^{5+}$ compounds will hydrolyse to $AsO_3^{3-}$, PO, DPO, $AsO_4^{3-}$, DPA and PA. It was checked that $AsCl_3$, $PhAsCl_2$ and $Ph_2AsCl$ hydrolyse to the same compounds in times less than those available for this reaction to take place in the column separations. The order of elution was:

| Eluent | Eluate |
|---|---|
| 1% ethanol in benzene | TPA, DPO |
| Abs. ethanol | (DPO tail), PO |
| 10% aq. ethanol | (PO tail), DPA |
| Water | (DPA tail) |
| 0·1% NaOH and 1% NaOH | PA, $AsO_3^{3-}$, $AsO_4^{3-}$ |
| 5% NaOCl | Inorganic arsenic (?) |

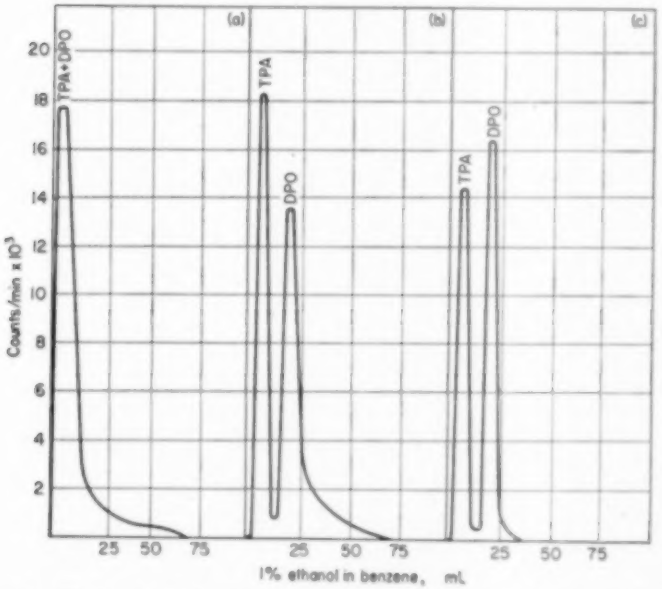



FIG. 1.—Elution curves for a mixture of TPA and DPO from alumina column:
(a) 5 ml portions collected
(b) 2 ml portions collected
(c) 2 ml portions collected after rechromatography of (a)

Differences in adsorption behaviour of the grades of alumina used for separation presumably account for the different sequence of elution observed in our case by comparison with the results of MADDOCK and SUTIN. Overlapping of fractions made the method unsuitable as such for analysis of reaction products. Thus the following additional procedures were developed. Resolution of the 1 per cent ethanol in benzene fraction was found possible by collection of 2 ml samples (Fig. 1).

The separation procedure was extended by paper chromatography of the following fractions:

(1) DPO + PO
(2) PO + DPA
(3) PA + $AsO_3^{3-}$ + $AsO_4^{3-}$

After extensive experiments with possible solvents the following systems were chosen:

(1) DPO + PO, benzene saturated with 1 per cent aq. acetic acid
(2) PO + DPA, butanol saturated with 5 per cent ammonia
(3) PA + $AsO_3^{3-}$ + $AsO_4^{3-}$, butanol saturated with 20 per cent acetic acid

TABLE 1.— R VALUES FOR As COMPOUNDS IN VARIOUS SOLVENTS ON WHATMAN NO. 1 PAPER

| Solvent | Substance | | | | | | |
|---|---|---|---|---|---|---|---|
| | $AsO_4^{3-}$ | $AsO_3^{3-}$ | PA | DPA | PO | DPO | TPA |
| Butanol sat. with 20% HAc | 0·1 | 0·47 | 0·77 | 0·9 | 0·9 | 0·9 | 0·9 |
| Butanol sat. with 5% $NH_3$ | 0 | 0·21 | 0·02 | 0·35 | 0·9 | 0·9 | 0·9 |
| Benzene sat. with 1% HAc | — | — | — | — | 0 | 0·9 | 0·9 |

$R_f$ values are shown in Table 1. Approximately 200 $\mu$gm of the substance in 0·01 ml benzene was placed on the strip and the chromatogram developed for 1–4 hr. Typical radiochromatograms are shown in Fig. 2.

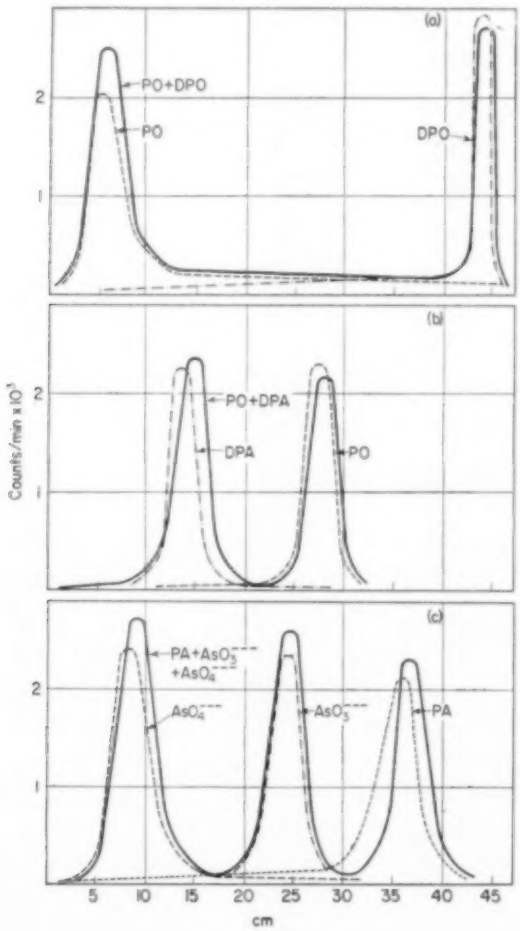



FIG. 2.—Paper radiochromatograms for mixtures of As compounds.
(a) PO + DPO — Bz sat. with 1% HAc
(b) DPA + PO — BuOH sat. with 5% $NH_3$
(c) PA + $AsO_4^{3-}$ + $AsO_3^{3-}$ — BuOH sat. with 20% HAc.

Vol. 12 1959/6

TABLE 2.—PER CENT ACTIVITIES OF FRACTIONS SEPARATED BY CHROMATOGRAPHY ON ALUMINA COLUMNS

| Exp. No. | 1% ethanol in bz. | | Abs. ethanol PO + + DPO | 10% aq. ethanol DPA + + PO | Water DPA | 0·1%+1% NaOH PA + $AsO_3^{--}$ + $^-$ + $ASO_4^{---}$ | 5%NaOCl As (?) |
|---|---|---|---|---|---|---|---|
| | I max. TPA (%) | II max. DPO (%) | (%) | (%) | (%) | (%) | % |
| 1 | 0 | 0 | 8·66 | 5·68 | 0·17 | 85·12 | 0·35 |
| 2 | 0·08 | 0 | 10·09 | 1·75 | 0·06 | 88·00 | 0 |
| 3 | 0 | 0 | 4·71 | 8·99 | 1·75 | 84·48 | 0 |
| 4 | 0 | 0 | 15·20 | 1·50 | 0·48 | 82·76 | 0 |
| 5 | 0 | 1·04 | 6·01 | 2·53 | 0·28 | 89·93 | 0·19 |
| 6 | 0·03 | 0·56 | 3·71 | 2·95 | 0·28 | 91·99 | 0·45 |
| 7 | 0·17 | 1·71 | 13·78 | 3·52 | 0·19 | 80·14 | 0·49 |
| 8 | 0·07 | 1·26 | 13·40 | 2·57 | 0·12 | 82·39 | 0·15 |
| 9 | 0·25 | 2·48 | 18·15 | 6·12 | 0·41 | 72·45 | 0·09 |
| 10 | 0·14 | 1·51 | 12·65 | 4·83 | 0·51 | 80·24 | 0·09 |
| 11 | 0·11 | 1·87 | 12·12 | 1·44 | 0 | 84·41 | 0 |
| 12 | 0·11 | 1·46 | 13·78 | 2·73 | 0·14 | 81·73 | 0 |
| | 0·08 ±0·2 | 0·99 ±0·85 | 11·02 ±4·43 | 3·72 ±2·37 | 0·37 ±0·47 | 83·64 ±5·11 | 0·15 ±0·25 |
| B. Irradiation of crystalline TPA (ca. $10^8$ neutrons/cm² per sec for ca. 3 × $T_{\frac{1}{2}}$) | | | | | | | |
| 1 | 8·12 | 12·19 | 11·97 | 12·95 | 2·95 | 47·23 | 4·61 |
| 2 | 10·10 | 16·10 | 12·56 | 13·43 | 2·26 | 41·81 | 3·73 |
| 3 | 11·02 | 16·26 | 18·08 | 17·99 | 2·57 | 28·03 | 6·00 |
| 4 | 7·87 | 9·15 | 16·85 | 16·76 | 2·03 | 41·93 | 5·32 |
| 5 | 10·91 | 12·64 | 17·60 | 15·88 | 1·53 | 36·29 | 5·12 |
| 6 | 9·43 | 10.94 | 16·60 | 16·04 | 3·64 | 37·31 | 6·00 |
| 7 | 9·81 | 10·87 | 15·77 | 16·31 | 2·29 | 35·61 | 9·28 |
| | 9·61 ±1·24 | 12·59 ±2·66 | 15·63 ±2·42 | 15·62 ±1·81 | 2·47 ±0·68 | 38·31 ±6·10 | 5·72 ±1·73 |
| C. Irradiation of 0·1 M TPA in benzene (ca. $10^9$ neutrons/cm² per sec for ca. 2 × $T_{\frac{1}{2}}$) | | | | | | | |
| 1 | 5·26 | 8·92 | 18·52 | 3·50 | 0·60 | 62·63 | 0·78 |
| 2 | 4·86 | 7·95 | 18·46 | 4·99 | 0·19 | 62·62 | 0·90 |
| 3 | 4·15 | 7·12 | 14·77 | 5·41 | 0·85 | 66·50 | 1·17 |
| 4 | 4·99 | — | — | — | — | 66·67 | 0·22 |
| 5 | 4·06 | 10·22 | 19·70 | 8·68 | 1·13 | 55·78 | 0·41 |
| 6 | 3·18 | 9·53 | 21·07 | 9·85 | 1·51 | 53·85 | 0·98 |
| | 4·41 ±0·77 | 8·75 ±1·24 | 18·50 ±2·34 | 6·48 ±2·63 | 0·85 ±0·63 | 61·34 ±5·39 | 0·74 ±0·36 |
| D. Irradiation of crystalline TPA (ca. $10^{12}$ neutrons/cm² per sec for ca. 1 × $T_{\frac{1}{2}}$) | | | | | | | |
| | 22·11 | 27·39 | 11·32 | 1·57 | 0·25 | 34·03 | 3·30 |

Vol. 12 59/60

TABLE 3.—PER CENT ACTIVITIES OF FRACTIONS SEPARATED BY PAPER CHROMATOGRAPHY

A. Irradiation of 0·1 M $AsCl_3$ in benzene (ca. $10^8$ neutrons/cm² per sec for ca. $3 \times T_{\frac{1}{2}}$)

| 0·1% NaOH fraction: Expt. No. | $AsO_4^{3-}$ | $AsO_3^{3-}$ | PA |
|---|---|---|---|
| 1 | 16·12 | 78·47 | 5·39 |
| 2 | 13·68 | 80·66 | 5·65 |
| 3 | 12·65 | 82·68 | 4·35 |
| 4 | 27·27 | 68·50 | 4·21 |
| 5 | 24·20 | 71·67 | 4·12 |
| | 18·78 ±6·57 | 76·39 ±6·05 | 4·74 ±0·72 |

B. Irradiation of crystalline TPA (ca. $10^8$ neutrons/cm² per sec for ca. $3 \times T_{\frac{1}{2}}$)

| 0·1% NaOH fraction: Expt. No. | $AsO_4^{3-}$ | $AsO_3^{3-}$ | PA |
|---|---|---|---|
| 1 | 24·83 | 61·45 | 13·69 |
| 2 | 23·81 | 61·41 | 14·77 |
| 3 | 29·07 | 54·29 | 16·62 |
| 4 | 30·05 | 58·11 | 11·83 |
| 5 | 30·46 | 56·43 | 13·10 |
| | 27·64 ±3·99 | 58·34 ±3·13 | 14·00 ±1·80 |

C. Irradiation of 0·1 M TPA in benzene (ca. $10^9$ neutrons/cm² per sec for ca. $2 \times T_{\frac{1}{2}}$)

| 0·1% NaOH fraction: Expt. No. | $AsO_4^{3-}$ | $AsO_3^{3-}$ | PA |
|---|---|---|---|
| 1 | 11·83 | 72·19 | 15·97 |
| 2 | 21·27 | 66·31 | 12·41 |
| | 16·55 ±6·68 | 69·25 ±4·15 | 14·19 ±2·52 |

| Abs. ethanol fraction: | | | 10% aq. ethanol fraction: | | |
|---|---|---|---|---|---|
| Expt. No. | PO | DPO | Expt. No. | PO | DPA |
| 1 | 64·82 | 35·18 | 1 | 82·64 | 17·36 |
| 2 | 63·54 | 36·46 | 2 | 81·00 | 19·00 |
| 3 | 65·20 | 34·80 | 3 | 59·32 | 40·68 |
| 4 | 67·22 | 32·78 | | | |
| | 65·19 ±1·52 | 34·81 ±1·52 | | 74·32 ±13·0 | 25·68 ±13·0 |

D. Irradiation of crystalline TPA (ca. $10^{12}$ neutrons/cm² per sec for ca. $1 \times T_{\frac{1}{2}}$)

| 0·1% NaOH fraction | $AsO_4^{3-}$ | $AsO_3^{3-}$ | PA |
|---|---|---|---|
| | 10·8 | 20·3 | 68·9 |
| Abs. ethanol fraction | PO | DPO | |
| | 100 | 0 | |
| 10% aq. ethanol fraction | PO | DPA | |
| | 9·7 | 90·3 | |

Vol. 12 1959/6

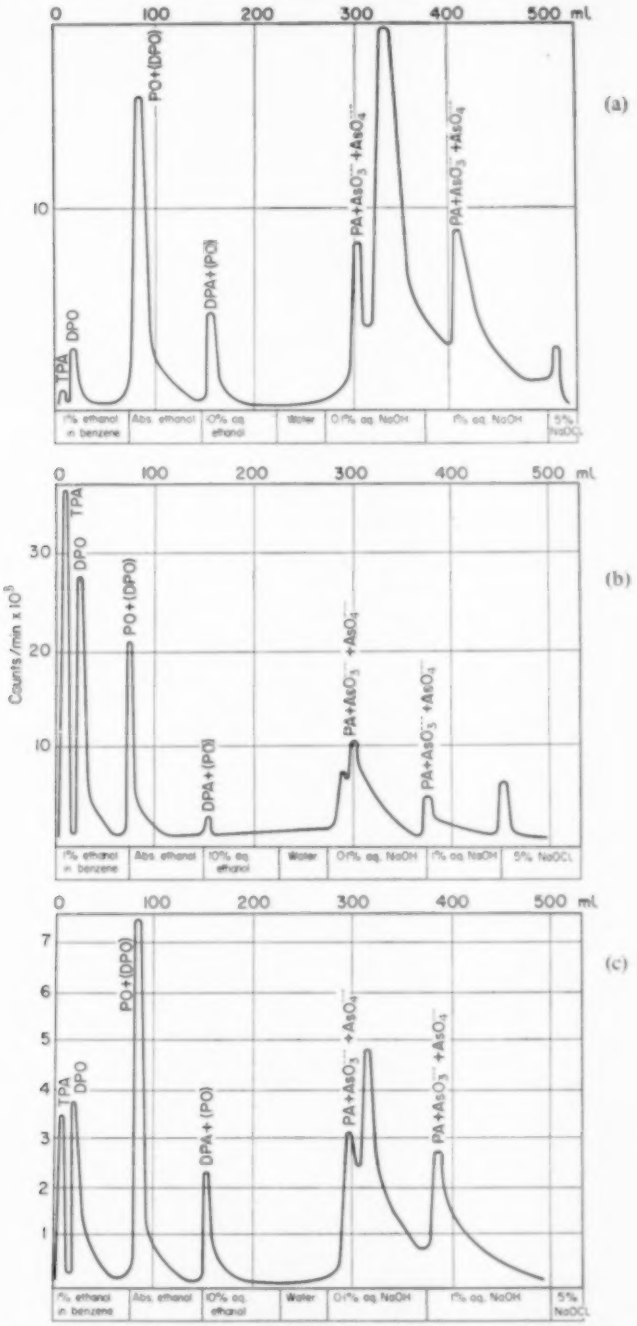



FIG. 3.—Typical elution curves of As compounds from irradiated mixtures:
(a) 0·1 M $AsCl_3$ in benzene irradiated
(b) Crystalline TPA irradiated
(c) 0·1 M TPA in benzene irradiated.

Vol. 12 59/60

The above combined procedures were used to analyse irradiated samples. Immediately after opening the irradiation capsule, the various inactive carriers were added, each in about 5 mg amount, and the contents well mixed. After transfer of 1 ml of irradiated solution or 200 mg TPA crystals to the column, 46 hr were allowed to elapse before elution, to allow hydrolysis to occur. The absolute ethanol, 10 per cent aq. ethanol and 0·1 per cent aq. NaOH fractions after collection were evaporated to about 0·5 ml and then separated further by paper chromatography.

TABLE 4.—PER CENT OF $^{76}$As ACTIVITY IN INDIVIDUAL As COMPOUNDS

A. Irradiation of 0·1 M $AsCl_3$ in benzene (ca. $10^8$ neutrons/cm$^2$ per sec for ca. $3 \times T\frac{1}{2}$)

| TPA (%) | DPO (%) | PO (%) | DPA (%) | PA (%) | $AsO_3^{3-}$ (%) | $AsO_4^{3-}$ (%) | As(?) % |
|---|---|---|---|---|---|---|---|
| 0·08 | 16·10 | | | 3·96 | 63·89 | 15·71 | 0·15 |

B. Irradiation of crystalline TPA (ca. $10^8$ neutrons/cm$^2$ per sec for ca. $3 \times T\frac{1}{2}$)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 9·61 | — | — | — | 5·36 | 22·35 | 10·58 | 5·72 |

C. Irradiation of 0·1 M TPA in benzene (ca. $10^9$ neutrons/cm$^2$ per sec for ca. $2 \times T\frac{1}{2}$)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 4·42 | 15·22 | 16·25 | 3·13 | 9·24 | 44·20 | 7·25 | — |

D. Irradiation of crystalline TPA (ca. $10^{12}$ neutrons/cm$^2$ per sec for ca. $1 \times T\frac{1}{2}$)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 22·11 | 27·39 | 11·3 | 1·7 | 23·1 | 3·7 | 7·2 | — |

The sample of crystalline TPA irradiated at $10^{12}$ neutrons/cm$^2$ per sec in the thermal column of "EWA", melted during irradiation.

## RESULTS

Results as percentage activities after numerical integration of areas of fractions are shown in Tables 2 and 3. All analyses of irradiated samples were done in duplicate. Errors quoted in Table 2 are standard errors for the series of determined percentage activities. These errors are greater than the appropriately summed statistical errors for the counts, so that the errors reveal variations due to variability of reactions, and more probably separations, rather than errors of radioactivity estimation. Percentage activities of individual fractions are calculated on the basis of summed activities of all eluted fractions.

Typical elution curves are shown in Fig. 3. Table 4 shows the distribution of $^{76}$As activity in individual arsenic compounds, combining the results from column and paper chromatography separations.

Vol. 12 1959/6

## DISCUSSION

It can be calculated from Tables 2 and 3 that the following gross distribution of $^{76}As$ activity is obtained:

| Substance irradiated | Dose rate ($n/cm^{-2}\,sec^{-1}$) | $AsPh_3$ (%) | $-AsPh_2$ (%) | $=AsPh$ (%) | $\equiv As$ (%) |
|---|---|---|---|---|---|
| $AsCl_3$ in bz | $10^8$ | 0·08 | 20·06 | | 79·6 |
| TPA in bz | $10^9$ | 4·4 | 18·4 | 25·5 | 51·5 |
| TPA crystals | $10^8$ | 9·6 | 51·7 | | 32·5 |
| TPA crystals* | $10^{10}$ | 9·3 | 12·5 | 35·1 | 30·8 |
| TPA crystals | $10^{12}$ | 22·1 | 29·1 | 34·5 | 10·9 |

* Results of MADDOCK and SUTIN[2]

There is good agreement between our results for crystalline TPA irradiated at $10^8$ neutrons/$cm^2$ per sec and the results of MADDOCK and SUTIN at $10^{10}$ neutrons/$cm^2$ per sec. This suggests that no interference from radiolysis occurs at dose rates up to $10^{10}$ neutrons/$cm^2$ per sec in this system.

*A priori* it could be expected that the following general mechanisms could be operative in the systems chosen for irradiation:

(a) Billiard-ball type collisions $^{76}As$–$^{75}As$. This mechanism in the case of irradiated TPA in benzene or crystalline TPA could lead to $^{76}As$ being present in $Ph_3As$, $Ph_2As$- and PhAs= compounds. However in the case of irradiated $AsCl_3$ in benzene such collisions can only yield inorganic $^{76}As$.

(b) Inelastic collisions of $^{76}As$ with benzene rings leading to production of radicals capable of combining with $^{76}As$ atoms, either before or after significant diffusion of the radicals has occurred. A similar result could perhaps be achieved by charge neutralization of $^{76}As$ by electron transfer from organic groups. These types of mechanism could lead to the production of $Ph_3As$, $Ph_2As$- and PhAs= compounds in all the irradiated systems. However, in the case of the system $AsCl_3$ in benzene it could be expected that billiard-ball collisions leading to formation of inorganic arsenic would be competitive.

(c) Formation of phenyl radicals by radiolysis, and combination of these radicals with cooled $^{76}As$ atoms to form organic compounds. This mechanism could be expected to give $Ph_3As$, $Ph_2As^-$ and PhAs= compounds in all the systems irradiated, and in addition would be expected to give a higher yield of organic $^{76}As$ at higher dose rates. However, it should be remembered that such a mechanism would be counteracted by the tendency of phenyl radicals to combine with eath other forming diphenyl. Doubt has previously been cast on the intervention of radicals from radiolysis of the medium in reactions of hot atoms.[15,16]

(d) Primary retention, i.e. failure to rupture Ph–As bonds by the $^{76}As$ atom during its initial recoil from $\gamma$-emission. Such primary retention giving organic $^{76}As$ could occur in irradiated crystalline TPA and TPA in benzene. Primary retention of this

[15] F. S. ROWLAND and W. F. LIBBY, *J. Chem. Phys.* **21**, 1495 (1953).
[16] G. LEVEY and J. E. WILLARD, *J. Amer. Chem. Soc.* **74**, 6161 (1953).

type may be even more probable in the case of irradiated $AcCl_3$ in benzene, leading to inorganic $^{76}As$, since the weight of the molecular residue is 105 in the case of $AsCl_3$ as compared with 225 in the case of TPA.

It might be suggested that the reduction of the percentage activity in organic As compounds when $AsCl_3$ in benzene is irradiated, by comparison with TPA in benzene, is due in large measure to the elimination of billiard-ball collisions between $^{76}As$ and $^{75}AsPh_3$ in the first case. In this connexion, however, it must be remembered that reduction of the percentage of $^{76}As$ in organic compounds could also be due to other causes, namely:

(i) $\gamma$-Radiolysis of $AsCl_3$ leading to formation of free chlorine capable of acting as a scavenger for organic radicals. Against this process would be the continual tendency for dissolved elementary chlorine to react with the elementary arsenic. In addition $AsCl_3$ may be itself a radical scavenger, phenyl radicals reacting directly with it to give chlorobenzene.

(ii) Exchange reaction between cooled $^{76}As$ atoms and $AsCl_3$.

The fact that organic arsenic activity arises when $AsCl_3$ in benzene is irradiated, suggests that a radical mechanism of the type given in hypothesis (b) must certainly be operative. In this connexion it should be pointed out that the system $AsCl_3$ in benzene presumably cannot show maximal operation of mechanisms of combination of $^{76}As$ with organic radicals because of the possible presence of free chlorine or $^{76}As$–$^{75}AsCl_3$ reactions, already described. From the present evidence more cannot be said as to the nature of the processes leading to radical formation, or the nature of the reactions of these radicals.

The ratio of arsenic atoms to phenyl rings in the case of TPA in benzene solutions was 1 : 116 and in the case of TPA crystals was 1 : 3. Thus it would seem that billiard-ball collisions leading to the formation of organic $^{76}As$ would be expected to be more pronounced in the second case. The smaller percentage of $^{76}As$ activity in $Ph_3As$, $Ph_2As$- and $PhAs=$ in the case of TPA in benzene might thus be considered as good evidence that the billiard-ball mechanisms play a significant part in the organic retention. From this point of view TPA in benzene would be a more favourable medium for operation of the radical mechanism than TPA crystals. On the other hand it should be pointed out that the intervention of a billiard-ball type mechanism is not necessary to explain the lower organic $^{76}As$ yield in the case of TPA in benzene, since a mechanism based on reaction with organic radicals might be also conceivably explain such a result, bearing in mind the difference of phase conditions. For example, a $^{76}As$ atom having lost a good deal of its recoil energy in elastic and inelastic collisions may find itself in a region of a high local radical concentration (radical nest).[6] In the case of TPA crystals, concentration of such radicals will be kept high up to the moment of dissolution in benzene, with a correspondingly high probability of their combining with the $^{76}As$ atoms. In the case of benzene solutions of TPA, the radical concentration in such a nest would be rapidly lowered. Then again it must be pointed out that according to the theoretical considerations advanced by LIBBY, organic retention of $^{76}As$ would be favoured in the TPA crystals as compared with TPA solutions in benzene, not only by the greater ratio of As atoms to benzene rings but also by the fact that conditions in the crystals are more favourable for resisting the escape of the $^{76}As$ atom from the site of the billiard-ball type collision before it

Vol. 12 1959/6

has combined with the organic radicals. It can be seen that many facts may be involved in this situation which the present results are insufficient to resolve, and further systematic studies will be made of the effects of these factors.

It can be seen that when crystalline TPA was irradiated at $10^{12}$ neutrons/cm$^2$ per sec there was a sharp increase in the percentage of $^{76}$As in organic compounds. The rise in retention could be explained either on the basis of extensive radical formation by $\gamma$-radiolysis of the TPA at this high irradiation level, or by increased density of radicals or radical nests formed by collisions of hot $^{76}$As or discharge of the latter by organic groups, in view of the higher rate of $^{76}$As production. The fact that the sample of crystalline TPA irradiated at $10^{12}$ neutrons/cm$^2$ per sec melted may influence the result by facilitating radical diffusion and thus combination with $^{76}$As during the irradiation.

With regard to the possibility that part of the organic $^{76}$As is due to primary retention it can be said on the basis of our results that the retention of 9·3 per cent as $AsPh_3$ observed by MADDOCK and SUTIN in irradiated TPA crystals cannot be due entirely to failure to rupture any Ph–As bonds during initial recoil, since this retention drops to 4·4 per cent for the solution of TPA in benzene. Further experiments with more diluted systems may still further reduce this figure.

It should be pointed out that in the case of $AsCl_3$ in benzene or TPA in benzene, hypochlorite did not elute any significant activity from the column, whereas an active fraction was eluted by this reagent in the case of TPA crystals (ca. 5 per cent of total eluted activity). The nature of this fraction is not at present known.

Vol.
12
59/60

*Acknowledgement*—The authors would like to thank the direction of the Joint Establishment for Nuclear Energy Research, Norway, for kindly allowing irradiations to be done in the thermal column of the reactor of that establishment. They would also like to thank the Reactor Group of the Institute of Nuclear Research for irradiations in "EWA", Dr. S. SIEKIERSKI for helpful discussions, and Mrs. R. OSINSKA for skilled technical assistance.

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 30 to 37. Pergamon Press Ltd. Printed in Great Britain.

# THE CONDITIONS FOR ELECTRODEPOSITION OF INSOLUBLE HYDROXIDES AT A CATHODE SURFACE: A THEORETICAL INVESTIGATION

P. G. HANSEN

Chemistry Department, Research Establishment Risø, Denmark

(*Received 5 February* 1959)

**Abstract**—The pH values obtained in the vicinity of a cathode surface where hydrogen evolution takes place are discussed using the concept of a diffusion layer. It is shown that a given current density $I$ determines a hydrogen ion concentration $C_{max}$ in the solution, above which no hydroxide deposition at the cathode can be expected to take place. The shape of the pH distribution makes it possible to define a hydroxyl ion layer, the thickness of which approaches zero as the hydrogen ion concentration approaches $C_{max}$. It is found that relatively high pH values (11–13) are easily obtained at a cathode surface, even in rather acid solutions. These results find some support in recent experimental work,[1] but further data are desirable.

Vol.
12
1959/6

A FREQUENTLY occurring problem in radiochemistry is the preparation of thin uniform sources of radioactive materials. For instance such sources are of great importance in nuclear spectroscopy and in assay work. In those cases where electroplating can be used, this technique is generally superior to others with respect to yield and uniformity. It has been found that a wide variety of elements which are too electropositive for deposition as metals can be deposited at an electrode by the use of suitable precipitation reactions.

Some of the procedures described for actinide elements have been based on a change of valency state for the metal being precipitated.[2,3] Most techniques, however, depend on a precipitation of insoluble compounds in the alkaline layer attaching to the cathode surface. The carbonates of Sr, Ba and Ra have thus been deposited from solutions containing carbon dioxide.[4,5,6] Hydroxide deposition has been of special importance, since this technique includes the numerous lanthanide and actinide elements. In this way Ac- and Th-sources have been prepared from aqueous solutions[5,7] and from alcohol–acetone solutions.[8] The paper by TÖDT[5] gives a qualitative discussion of the conditions for the electrolytical deposition of Ra, Ac

[1] G. LANGE, G. HERRMANN and F. STRASSMANN, *J. Inorg. Nucl. Chem.* **4**, 146 (1957).
[2] A. C. GRAVES and D. K. FROMAN, *Miscellaneous Physical and Chemical Techniques of the Los Alamos Project* pp. 22–36. McGraw-Hill, New York (1952).
[3] H. W. MILLER and R. J. BROUNS, *Analyt. Chem.* **24**, 536 (1952).
[4] O. VON BAYER, O. HAHN and L. MEITNER, *Phys. Z.* **16**, 6 (1915).
[5] F. TÖDT, *Z. Phys. Chem.* **113**, 329 (1924).
[6] G. HERRMANN, *J. Inorg. Nucl. Chem.* **7**, 129 (1958).
[7] L. MEITNER, *Phys. Z.* **12**, 1094 (1911).
[8] S. COTELLE and M. HAISSINSKY, *C. R. Acad. Sci., Paris* **206**, 1644 (1938).

and Th. Precipitation of macro amounts was used by DENNIS and LEMON[9] in an attempt to separate rare earth elements. DEDOV and KOSYAKOV[10] deposited Pu, Am and Cm from neutral or weakly acid solutions in water or mixtures of alcohol, acetone and water. Preliminary experiments were carried out with Ce and Sm. KO[11,12] deposited Th, U, Np, Am and Cm from aqueous solutions containing ammonium formate (e.g. buffered to a pH about 3·6). The increase in pH during the electrolysis due to the anodic decomposition of formic acid was reported to facilitate the precipitation. A promethium source was prepared by electrolysis in 98 per cent ethylenediamine[13] under conditions closely resembling those necessary for the preparation of free rare earth metal. Electrodeposition of yttrium from weak nitric acid was reported by LANGE *et al.*,[1] who used this technique for separating yttrium from strontium. High yields of carrier-free $^{90}Y$ and a very good separation from $^{90}Sr$ were obtained. It is interesting to note that the deposition rates were found to increase with decreasing pH, although no deposition was observed below pH 1. Under different conditions an effect opposite to this was observed by DEDOV and KOSYAKOV.[10] In connection with recent research in nuclear spectroscopy the preparation of $\beta$-sources of lanthanide and actinide elements by means of electrolysis has been described. Rare earths have been deposited from pyridine[14] and from ethyl alcohol,[15] and actinides from aqueous solutions of ammoniumbisulphate.[16]

In view of the numerous procedures described in the literature, it was felt that an investigation of the conditions for formation of hydroxide precipitates at a cathode might be of interest. The present paper attempts a theoretical approach to this problem with emphasis on the steady state diffusion of hydrogen and hydroxyl ions at the cathode surface. The results obtained are summarized in section (3) "Discussion".

Vol. 12 59/60

## 1. THE DIFFUSION EQUATIONS

The hydroxide formed at the cathode is presumably in equilibrium with hydroxyl ions and metal ions. Thus it is known that a deposit formed from acid solution will dissolve, if the current is turned off while the electrodes remain in the solution. Therefore it is of interest to calculate the pH obtained at the cathode surface during the electrolysis. This pH must be the result of a competition between hydrogen ions from the solution and hydroxyl ions formed at the cathode surface. The problem is somewhat related to the "concentration overpotential" encountered in electrolysis.[17a]

A convenient tool when treating problems at an electrode is the diffusion layer.[17b] Diffusion of ions to and from the cathode surface takes place in this layer (which is assumed at rest and of a well defined thickness $l$), while the rest of the liquid is assumed well stirred and of a constant composition. Using this concept the following set of

(9) L. M. DENNIS and B. J. LEMON, *J. Amer. Chem. Soc.* **37**, 131 (1915).
(10) V. B. DEDOV and V. N. KOSYAKOV, *Proceedings of the 1st International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 369. United Nations, New York (1956).
(11) R. KO, HW-32673 (1954).
(12) R. KO, *Nucleonics* **14**, No. 7, 74 (1956); **15**, No. 1, 72 (1957).
(13) J. E. GATES and D. F. EDWARDS, *Nucleonics* **13**, No. 12, 57 (1955).
(14) J. W. MIHELICH, T. J. WARD and K. P. JACOB, *Phys. Rev.* **103**, 1285 (1956).
(15) B. V. BOBYKIN and K. M. NOVIK, *Dokl. Akad. Nauk SSSR* **115**, 263 (1957).
(16) W. G. SMITH, UCRL-2974 (1955).
(17) See e.g. J. J. LINGANE, *Electroanalytical Chemistry* (a) p. 167; (b) p. 193. Interscience, New York (1953).

equations can be obtained (a list of symbols is given in Table 1). An inert salt is assumed to be present in the solution in order to insure electro-neutrality. For simplicity only the one-dimensional problem is treated. Nevertheless the results may be expected to be of a rather general validity due to the smallness of $l$ compared to normal cathode dimensions.

TABLE 1.—LIST OF SYMBOLS

| | |
|---|---|
| $a, b, c, d$ | Arbitrary constants—see equations (4) and (5) |
| $c_H, c_{OH}$ | Concentration of hydrogen and hydroxyl ions in the diffusion layer |
| $C$ | Hydrogen ion concentration in the solution |
| $D_H, D_{OH}$ | Diffusion coefficients for the hydrogen and hydroxyl ions |
| $I$ | Current density at the cathode |
| $K_W$ | Ion product for water |
| $l$ | Thickness of the diffusion layer |
| $l_{OH}$ | Thickness of the hydroxyl ion layer |
| $S(x)$ | "Source" term describing the disappearance of hydroxyl and hydrogen ions in the diffusion layer |
| $x$ | Distance from the cathode |

In the steady state $c_H$ and $c_{OH}$ must obey the following equations:

$$\frac{dc_H}{dt} = D_H \frac{d^2c_H}{dx^2} + S(x) = 0 \tag{1}$$

$$\frac{dc_{OH}}{dt} = D_{OH} \frac{d^2c_{OH}}{dx^2} + S(x) = 0 \tag{2}$$

where the $S$-terms describe the disappearance of hydroxyl- and hydrogen-ions through combination with each other. For stoicheiometric reasons these terms must be identical. A relation between $c_H$ and $c_{OH}$ is:

$$c_H c_{OH} = K_W \tag{3}$$

Integrating equations (1) and (2) and using equation (3) one obtains:

$$c_H = ax + b + \left[(ax + b)^2 + \frac{D_{OH}}{D_H} K_W\right]^{\frac{1}{2}} \tag{4}$$

$$c_{OH} = cx + d + \left[(cx + d)^2 + \frac{D_H}{D_{OH}} K_W\right]^{\frac{1}{2}} \tag{5}$$

where $a$, $b$, $c$ and $d$ are constants that can be expressed in terms of integration constants and the $D$'s. These constants can be found from the boundary conditions. Continuity at the diffusion layer–liquid interface gives:

$$c_H = C \quad (\text{for } x = l) \tag{6}$$

Since the rate of production of hydroxyl ions must equal the rate of removal one must have:

$$I = -D_{OH} \frac{dc_{OH}}{dx} \quad (\text{for } x = 0) \tag{7a}$$

Vol 12 1959/

## 2. APPROXIMATE SOLUTION

If the current at the boundary between the diffusion layer and the liquid is carried mainly by hydrogen ions, the boundary condition (7a) can be replaced by the analogous expression:

$$-I = -D_H \frac{dc_H}{dx} \quad (\text{for } x = l) \tag{7b}$$

Apparently this is true if $C^2 \gg K_W$. Inserting (4) into (6) and (7b) gives:

$$a = \frac{1}{2}\left(\frac{I}{D_H} + \frac{ID_{OH}K_W}{C^2 D_H^2}\right) \tag{8}$$

$$b = \frac{1}{2}\left(C - \frac{D_{OH}K_W}{D_H C} - \frac{Il}{D_H} - \frac{IlD_{OH}K_W}{C^2 D_H^2}\right) \tag{9}$$

Since it has been assumed that $1 \gg K_W/C^2$, three terms in equations (8) and (9) can safely be neglected. Therefore $a$ and $b$ can simply be expressed as follows:

$$a = I/2D_H \tag{10}$$

$$b = \tfrac{1}{2}(C - Il/D_H) \tag{11}$$

The complete pH distribution within the diffusion layer can now be calculated from equation (4). As a numerical example Fig. 1 shows the pH as a function of $x$ for different values of $C$, with $I = 1{\cdot}03 \times 10^{-3}$ meq/cm²sec corresponding to 100 mA/cm² current density.

From Fig. 1 it is seen that the curves, in which an inflexion point occurs, with good accuracy define a "hydroxyl ion layer" with thickness $l_{OH}$. Taking the inflexion point as a measure of $l_{OH}$ one obtains:

$$l_{OH} = l - CD_H/I \tag{12}$$

When the inflexion point moves across $x = 0$ (with increasing $C$) a rapid change in the shape of the pH curve takes place. One sees that only for $l_{OH} > 0$ are high pH values obtained at the cathode. The hydrogen ion concentration in the liquid must therefore be smaller than $C_{max}$ in order that hydroxide precipitation can take place, where $C_{max}$ is given by:

$$C_{max} = Il/D_H \tag{13}$$

Correspondingly equation (13) defines a minimum current density if $C$ is considered fixed. In this case equation (13) is formally related to the "limiting current" encountered in electrolysis (see e.g. ref. 17b).

For $C_{max} > C$ and $(C_{max} - C)^2 \gg 4K_W$ the hydrogen ion concentration at the cathode can be expressed as:

$$c_H = \frac{D_{OH}K_W}{Il - CD_H} \quad (\text{for } x = 0) \tag{14}$$

This expression is obtained by expanding the square root term in equation (4) as a Taylor series using the two first terms.



Vol. 12 59/60

For small values of $C$ the hydroxyl ion concentration at the cathode is proportional to the current density. In the range of current densities normally applied (1–100 mA/cm²) high pH values can be obtained (10·8–12·8). This should suffice for most precipitation reactions. Rare earth hydroxides have solubility products[18] in the range $10^{-19}$–$10^{-24}$ moles⁴/l⁴. For a $10^{-10}$ M La-solution the solubility product will thus be exceeded at pH 11.

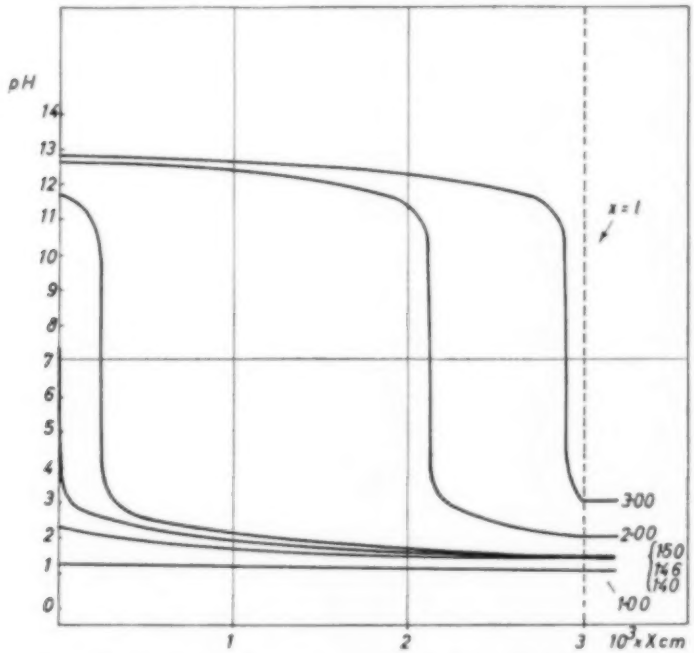



FIG. 1.—The pH values in the diffusion layer are shown as a function of $x$, the distance from the cathode. Curves are shown for various pH values in the solution. The following numerical values have been used:

$$I = 1{\cdot}03 \times 10^{-3} \text{ meq/cm}^2\text{sec} \sim 100 \text{ mA/cm}^2$$
$$D_H = 9{\cdot}0 \times 10^{-5} \text{ cm}^2/\text{sec};\ D_{OH} = 5{\cdot}1 \times 10^{-5} \text{ cm}^2/\text{sec}$$
$$l = 3 \times 10^{-3} \text{ cm};\ K_W = 10^{-14} \text{ moles}^2/\text{l}^2$$

## 3. DISCUSSION

The results obtained can be summarized as follows:

(a) Given the current density $I$, the maximum hydrogen ion concentration $C_{max}$ (in the liquid) at which hydroxide deposition at the cathode can take place is given by equation (13).

(b) The pH in the diffusion layer varies in such a manner that a hydroxyl ion layer with thickness $l_{OH}$ can be defined (as long as $C_{max} > C$). $l_{OH}$ is given by equation (12).

(c) pH at the cathode is a rapidly varying function of $C$ for $C \simeq C_{max}$. If $C_{max} > C$ and $(C_{max} - C)^2 \gg 4K_W$ the hydrogen ion concentration at the cathode surface is given by equation (14).

[18] C. SNEED and M. BRASTED (Editors), *Comprehensive Inorganic Chemistry* Vol. IV, p. 170. Van Nostrand, New York (1955).

Fig. 2A shows the dependence of $l_{OH}$ on $C$ for fixed values of $I$ and $l$. Fig. 2B shows for the same set of conditions the pH at the cathode surface as a function of $C$. It is seen that as $C$ approaches $C_{max}$, the pH stays almost constant while $l_{OH}$ diminishes. Presumably the formation of metal hydroxide begins at the distance $l_{OH}$

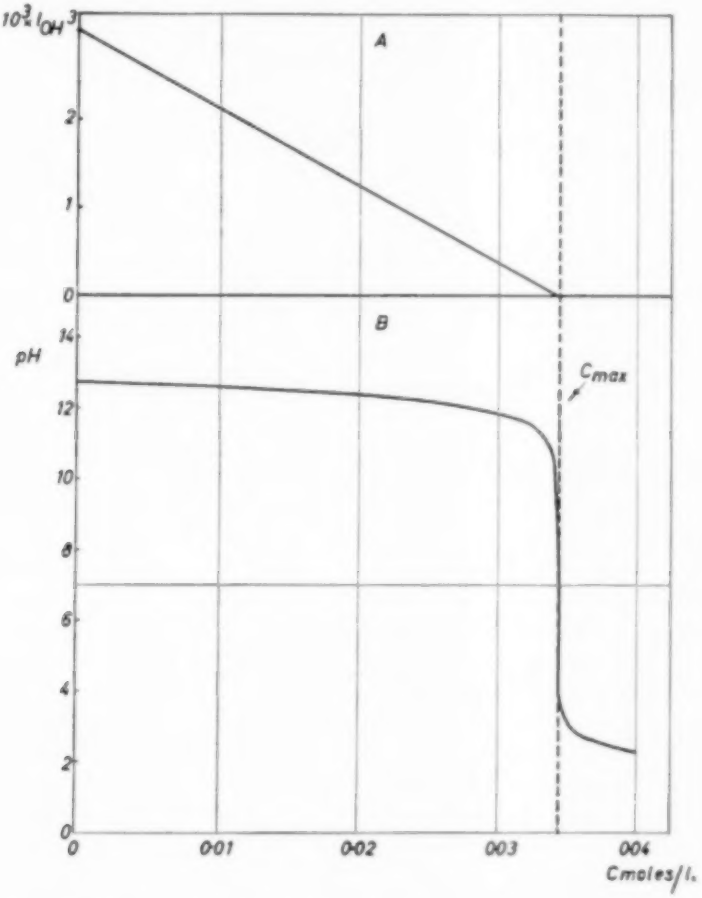



FIG. 2.—A. The thickness $l_{OH}$ of the hydroxyl ion layer as a function of $C$, the hydrogen ion concentration in the solution.
For $C > C_{max}$ $l_{OH}$ is not defined.
B. The pH at the cathode surface versus $C$.
The numerical values used are the same as in Fig. 1.

from the cathode. It seems likely that the rate determining process in the electrodeposition of insoluble hydroxides is the transport of hydroxide through the "hydroxyl ion layer". In this case one will expect increasing deposition rate with decreasing $l_{OH}$ —that is with $C$ approaching $C_{max}$.

The existing experimental evidence does not suffice for a detailed check on the predictions given above. Best suited for a comparison is the investigation by LANGE *et al.*[1] These authors worked with aqueous nitric acid solutions. Strontium nitrate

Vol. 12 59/60

was added so the solutions were $1{\cdot}87 \times 10^{-3}$ M with respect to $Sr^{2+}$. Although this amount is too small to act as a constant salt medium, it still is a feature which may help to compensate for charge and conductivity effects. Unfortunately the current density is not known for most of these experiments; usually, only the applied voltage is given. In the following, the predictions (a)–(c) are compared with available experimental results.

(a) The deposition of yttrium[1] was found to begin at a pH about 1·5 for an applied voltage of 12 V. Assuming this to correspond to a current density about 100 mA/cm² one obtains from equation (13) for $l = 3 \times 10^{-3}$cm: $C_{max} = 3{\cdot}4 \times 10^{-2}$ corresponding to pH 1·46. It was furthermore found that at pH 2·54, the deposition started at a current density about 10 mA/cm². In this case one obtains $C_{max} = 3{\cdot}4 \times 10^{-3}$, that is pH 2·46. The agreement between experimental and predicted values is thus relatively good. It must be taken into account that the value for $l$ was chosen rather arbitrarily (see e.g. ref. 19 for some experimental values), and that the two measurements quoted above were carried out at different temperatures.

(b) The deposition rates were found[1] to increase with decreasing pH when the applied voltage was kept constant. This is qualitatively in agreement with what might be expected from the decrease in thickness of the hydroxyl ion layer. DEDOV and KOSYAKOV,[10] however, found a pH dependence for the electrodeposition of Am, which is opposite to the one discussed above. The situation is thus not at all clear.

The curves shown in Fig. 1 would tend to indicate a constant deposition rate at the higher pH values since $l_{OH} \simeq l$. Experimentally[1,10] this was not found. Two factors, however, must be taken into account. Firstly a considerable anodic deposition was observed[1] starting at pH 3·5 and reaching a maximum at pH 5–7. Competition from processes of this kind may well influence the deposition rate at the cathode. Secondly the computed pH distributions should be regarded with caution in regions remote from the cathode, since the calculations are based on the assumption of a diffusion layer at rest with a sharp boundary. This assumption should be taken only as a convenient way of averaging results, although it probably will result in quite accurate predictions for phenomena taking place close to the cathode. Predictions with respect to phenomena distant from the cathode can hardly have anything but qualitative significance.

(c) The satisfactory deposition of many lanthanide and actinide elements—also in tracer amounts—goes well with the result that pH values between 11 and 13 can be obtained easily at a cathode where hydrogen evolution takes place.

Unfortunately the present treatment does not include anything but qualitative suggestions with regard to the deposition rate. Empirically it has been found[10] that the deposition curves have approximately an exponential shape. This would however be true as long as the amount deposited per unit time is proportional to the amount present in the solution. Presumably the deposition rate will be dependent on factors such as the diffusion rate of the free metal ion, the thickness of the hydroxyl ion layer and the speed of motion of the metal-hydroxyl complex (may be as a radiocolloid) through this layer. Furthermore the adherence of the precipitate to the electrode must be taken into account (see e.g. refs. 5 and 12).

[19] J. FAHLAND, G. HERRMANN and F. STRASSMANN, *J. Inorg. Nucl. Chem.* **7**, 201 (1958).

Vol. 12 1959/6

## 4. CONCLUSION

The theory presented above may possibly explain some of the features connected with the electrodeposition of insoluble hydroxides. It is hoped that the results will become useful to predict conditions for such processes. Further experimental data are needed in order to test the validity of the hypothesis presented. A crucial test is of course the applicability of equation 13.

In principle it should be possible to apply the scheme used here also to other electrodeposition processes, where a precipitating agent is generated at an electrode. Deviations from the trivial case should appear where the precipitating agent is removed continuously through a reaction with some component in the solution.

Very little is known about the deposition rate. Further information would be desirable in view of the great practical interest in obtaining faster procedures.

ol.
12
9/60

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 38 to 44. Pergamon Press Ltd. Printed in Great Britain.

# ELECTROMETRIC STUDIES ON SILVER ARSENITES

RAM SAHAI SAXENA and C. S. BHATNAGAR

Chemical Laboratories, Government College, Kota (Rajasthan), India

(*Received* 23 *March* 1959)

**Abstract**—The formation and composition of silver arsenites obtained by the addition of $AgNO_3$ to $NaAsO_2$ and vice versa at pH 9·85, 11·25 and 12·28 have been studied potentiometrically using a silver electrode in conjunction with a saturated calomel electrode and $KNO_3$ salt bridge. Three definite arsenite compounds are formed having the molecular formulae $Ag_2O{\cdot}As_2O_3$, $2Ag_2O{\cdot}As_2O_3$; $3Ag_2O{\cdot}As_2O_3$ at pH 9·85, 11·25 and 12·28, respectively. The proportion of $Ag_2O$ increases with the amount of alkali used in the preparation of the sodium arsenite solution. The potentiometric titration curves are regular in form, a pronounced maximum in $dE/dC$ occurs at the end-point, and the results are accurate and reproducible.

A SURVEY of the literature reveals that there are few references to silver arsenites and most workers have based their conclusions on analytical investigations. SIMON[1] observed that an aqueous solution of $As_2O_3$ gave a white turbitity with $AgNO_3$, which turned yellow in presence of alkali. FILHOL[2] reported the formation of a normal arsenite on the addition of an aqueous solution of $As_2O_3$ to an ammoniacal solution of $AgNO_3$. According to PASTEUR[3] silver pryoarsenite $Ag_4As_2O_5$ is formed when an alkali pyroarsenite is added to an aqueous solution of $AgNO_3$, but the salt could not be obtained in a pure state. SANTOS[4] obtained $Ag_3AsO_3$ as a yellow precipitate with an alkali orthoarsenite and mentioned that mono- and di-hydrogen arsenites may also be obtained by mixing $AgNO_3$ and sodium arsenite in suitable molecular proportions; the normal arsenite was almost insoluble in water, but dissolved in presence of acids. KUHN[5] reported that the salt was also soluble in excess alkali and that if the solution was heated, silver was precipitated. MAYER[6] observed that the product of interaction of $KAsO_2$ and $AgNO_3$ is $Ag_3AsO_3$, and this view was further supported by BRAND and ROSENKRANZ.[7]

The investigation of arsenites is made difficult by the adsorption of arsenite by metallic hydroxides; the conversion of orthoarsenite to pyro- and meta-arsenite takes place with much greater ease and these dissolve in excess alkali or acid.[8] Consequently analytical methods have failed to give a correct view of their composition.

(1) J. F. SIMON, *Pogg. Ann.* **40**, 419 (1837).
(2) E. FILHOL, *J. Pharm. Chim.* **14**, 331 (1848).
(3) L. PASTEUR, *J. Pharm. Chim.* **14**, 331 (1848); *Ann.* **68**, 309 (1848).
(4) J. R. SANTOS, *C.R. Acad. Sci., Paris* **144**, 641 (1907).
(5) O. B. KUHN, *Arch. Pharm.* **2**, 69, 267 (1852).
(6) A. MAYER, *Ann. Sci. Univ. Jasse* Part I, *Maths. Phys. Chem.* **24**, 201-210 (1938).
(7) K. BRAND and E. ROSENKRANZ, *Pharm. Zentral. Halle* **79**, 537-542 (1938).
(8) F. EPHRAIM, *Textbook of Inorganic Chemistry* p. 745 (translated by P. C. L. THORNE and E. R. ROBERTS). Gurney and Jackson, London (1949).



Vol. 12 1959/6

TABLE 1.—SUMMARY OF RESULTS OF POTENTIOMETRIC TITRATION

| Molarity of solutions | | Equivalence point (ml) | | | Formula |
|---|---|---|---|---|---|
| | | Calculated | Observed from $dE/dC$ in presence of alcohol | | |
| $NaAsO_2$ | $AgNO_3$ | | 0% | 20% | |
| **Direct titrations** | | | | | |
| $NaAsO_2$ soln. at pH 9·85 added to 20 ml of $AgNO_3$ soln. at pH 6·60 (Fig. 1, Curves 1–4) | | | | | |
| M/10 | M/50 | 4·0 | 4·05 | 4·0 | $AgAsO_2$ or |
| M/50 | M/200 | 5·0 | 5·04 | 4·98 | $(Ag_2O{\cdot}As_2O_3)$ |
| M/200 | M/600 | 6·66 | 6·70 | 6·65 | |
| $Na_4As_2O_5$ ($2NaAsO_2 + 2NaOH$) soln. at pH 11·25 added to $AgNO_3$ soln. at pH 6·60 (Fig. 2, Curves 1–4) | | | | | |
| M/10 | M/10 | 5·0 | 4·85 | 4·96 | $Ag_4As_2O_5$ or |
| M/40 | M/50 | 4·0 | 3·92 | 3·96 | $(2Ag_2O{\cdot}As_2O_3)$ |
| $Na_3AsO_3$ ($2NaAsO_2 + 4NaOH$) soln. at pH 12·28 added to $AgNO_3$ soln. at pH 6·60 (Fig. 3, Curves 1–4) | | | | | |
| M/50 | M/75 | 4·40 | 4·36 | 4·42 | $Ag_3AsO_3$ or |
| M/10 | M/10 | 6·66 | 6·58 | 6·64 | $(3Ag_2O{\cdot}As_2O_3)$ |
| **Reverse titrations** | | | | | |
| $AgNO_3$ soln. at pH 6·60 added to $NaAsO_2$ soln. at pH 9·85 (Fig. 4, Curves 5–8) | | | | | |
| M/50 | M/10 | 4·0 | 3·90 | 3·95 | $AgAsO_2$ or |
| M/400 | M/100 | 5·0 | 4·94 | 4·98 | $(Ag_2O{\cdot}As_2O_3)$ |
| $AgNO_3$ soln. at pH 6·60 added to 20 ml of $Na_4As_2O_5$ ($2NaAsO_2 + 2NaOH$) soln. at pH 11·25 (Fig. 5, Curves 5–8) | | | | | |
| M/200 | M/10 | 4·0 | 3·85 | 3·95 | $Ag_4As_2O_5$ or |
| M/800 | M/50 | 5·0 | 4·88 | 4·96 | $(2Ag_2O{\cdot}As_2O_3)$ |
| $AgNO_3$ soln. at pH 6·60 added to 20 ml of $Na_3AsO_3$ ($2NaAsO_2 + 4NaOH$) soln. at pH 12·28 (Fig. 6, Curves 5–8) | | | | | |
| M/400 | M/25 | 3·75 | 3·55 | 3·65 | $Ag_3AsO_3$ or |
| M/100 | M/10 | 6·0 | 5·80 | 5·92 | $(3Ag_2O{\cdot}As_2O_3)$ |

In view of the difficulties associated with analytical work, and in the absence of any decisive views on the composition of silver arsenites, it was considered worth while to make a detailed and systematic study of the formation of silver arsenites at definite hydrogen ion concentrations by applying physicochemical methods which have given more conclusive evidences on the composition of complexes.[9] In this paper the results of potentiometric titrations are discussed.

[9] R. S. SAXENA, *Z. Anal. Chem.* **160**, 353, 194 (1958); *Naturwissenchaften* **45**, 128, 438, 11 (1958); *Anal. Chim. Acta* **19**, 402 (1958); *J. Indian Chem. Soc.* **35**, 665, 830 (1958); *J. Sci. Ind. Res. (India)*, **17B**, 505 (1958); *Curr. Sci. (India)* **27**, 487 (1958).

## EXPERIMENTAL

Merck's guaranteed extra pure reagents ($AgNO_3$ and $NaAsO_2$) were used. Silver nitrate solutions were estimated by Volhard's method and sodium arsenite solution was standardized by titrating against a standard iodine solution. The pH of $NaAsO_2$ solutions was measured with a glass electrode and buffer solutions. Suitable amounts of NaOH were added to $NaAO_2$ solutions in definite molecular proportions to vary the pH.

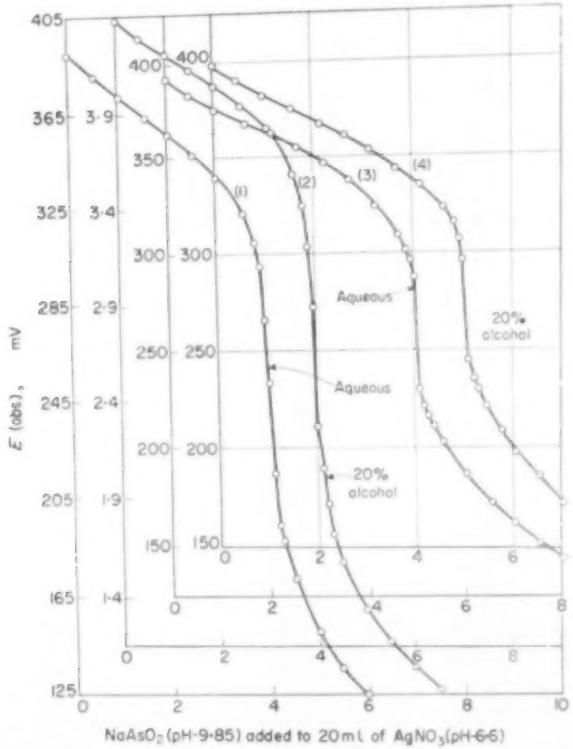



FIG. 1.—Direct titrations. Curve (1): (M/10)$NaAsO_2$; Curve (2): (M/50)$AgNO_3$; Curve (3): (M/50)$NaAsO_2$ and Curve (4): (M/50)$AgNO_3$.

Using different concentrations of $AgNO_3$ and sodium arsenite solutions at pH 9·85, 11·25 and 12·28, potentiometric titrations were performed by both direct and inverse methods, i.e. when sodium arsenite solution from a micro-burette was added to $AgNO_3$ solution in the electrode cell and vice versa.

For precise and steady e.m.f. measurements a platinum gauze electrode was used. This was electrolytically coated with silver at a low current density (current 2–10 mA) in a bath of pure potassium silver cyanide, and was used as an indicator electrode in conjunction with a saturated calomel electrode, the connexion between the calomel half-cell and the titration vessel being through a saturated $KNO_3$ salt bridge. The electrode cell was immersed in an electrically-maintained thermostat. The solution was continuously stirred by an electrically-driven stirrer and the e.m.f. was measured on a Cambridge (null-deflexion type) pH meter. Curves were plotted of $E$(obs) vs. the volume of the titrant added in ml. A sharp deflexion in the curve occurs at the end-point, marked by a pronounced maximum in $dE/dC$. Titrations were also carried out in presence of varying concentrations of ethanol. 20 ml of the reagent was taken in the cell each time.

Vol. 12 1959/6

## DISCUSSION

The pH of a stock solution of $NaAsO_2$ was found to be 9·85. By progressive additions of calculated amounts of NaOH solution, the pH is gradually increased, and when NaOH is mixed with $NaAsO_2$ in the molecular ratio 1:1 and 2:1, the corresponding compounds are $Na_4As_2O_5$ (sodium pyroarsenite) and $Na_3AsO_3$ (sodium orthoarsenite), and the pH of their solutions were found to be 11·25 and 12·28 respectively.

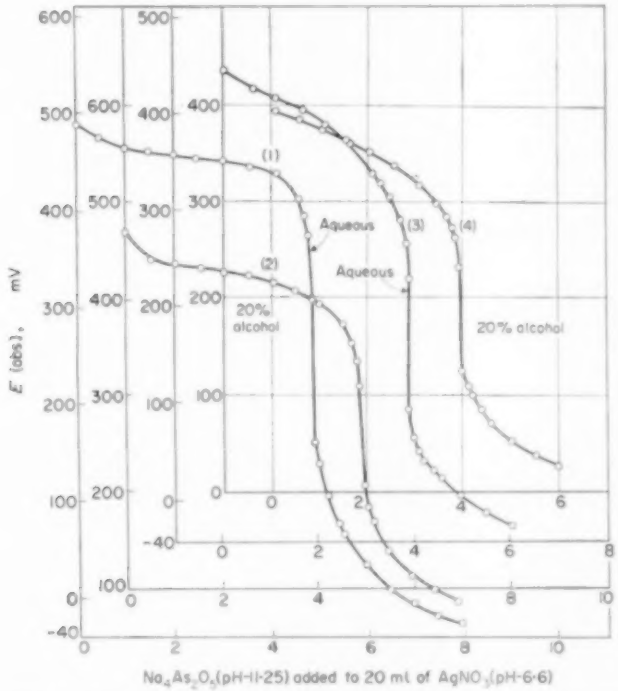



FIG. 2.—Direct titrations. Curve (1): (M/10)$Na_4As_2O_5$; Curve (2): (M/10)$AgNO_3$; Curve (3): (M/40)$Na_4As_2O_5$ and Curve (4): (M/50)$AgNO_3$.

It is clear from Figs. 1 and 4 and from the summary of observations in Table 1 that when $AgNO_3$ solution is added to $NaAsO_2$ solution (pH 9·85) or vice versa, and the potential is plotted against the volume of the titrant in ml, sharp deflexion occurs when the molecular ratio of $AgNO_3$ : $NaAsO_2$ is 1 : 1, corresponding to the formation of silver metaarsenite, $AgAsO_2$ or $Ag_2O{\cdot}As_2O_3$. At pH 11·25, the potentiometric titrations between $AgNO_3$ and $Na_4As_2O_5$ suggest the formation of a bright yellow compound silver pyroarsenite having the molecular formula $Ag_4As_2O_5$ (Figs. 2 and 5). The titrations of $AgNO_3$ and $Na_3AsO_3$ at pH 12·28 show a sharp break at the equivalence point, and the precipitate formed corresponds very closely to yellow silver ortho-arsenite, $Ag_3AsO_3$ or $3Ag_2O{\cdot}As_2O_3$.

In direct titrations with silver nitrate as titre, a yellowish granular precipitate is formed which begins to assume a colloidal form on the addition of excess of $NaAsO_2$

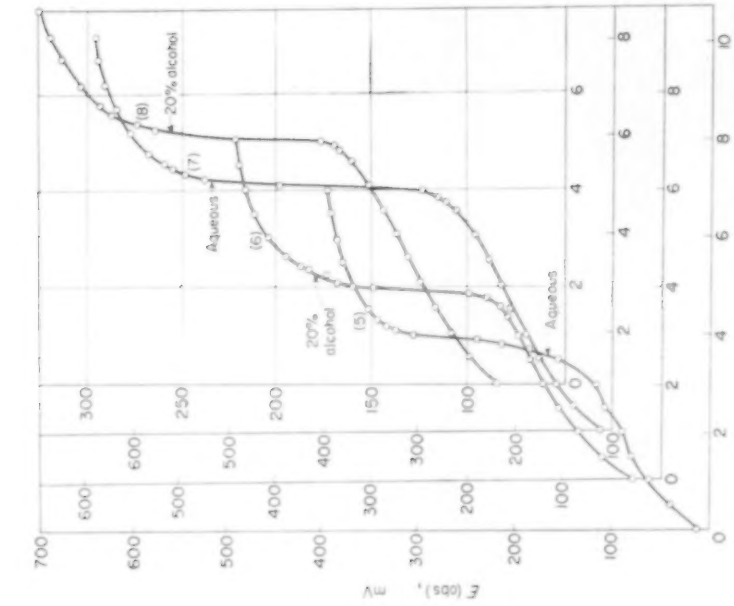



FIG. 4.—Reverse titrations. Curve (5): (M/10)$AgNO_3$; Curve (6): (M/50)$NaAsO_2$; Curve (7): (M/100)$AgNO_3$ and Curve (8): (M/400)$NaAsO_2$.

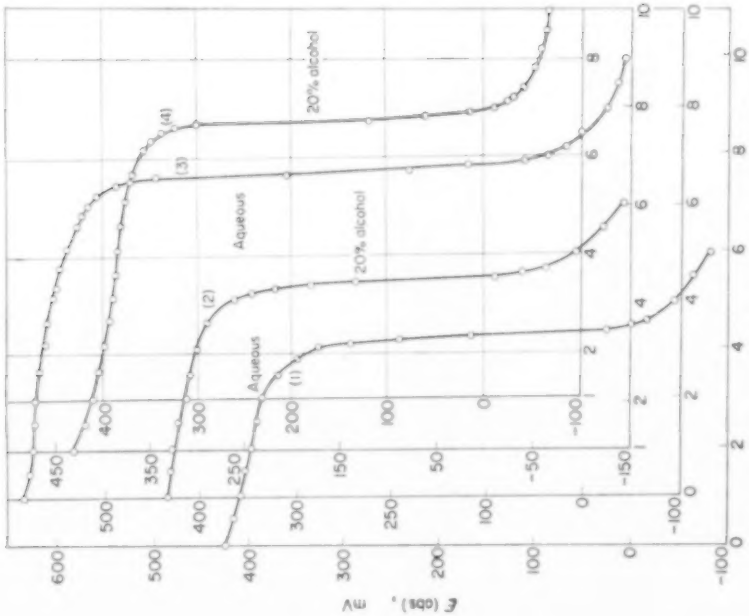



FIG. 3.—Direct titrations. Curve (1): (M/50)$Na_3AsO_3$; Curve (2): (M/75)$AgNO_3$; Curve (3): (M/10)$Na_3AsO_3$ and Curve (4): (M/10)$AgNO_3$.

Vol. 12 1959/60

after the end-point; when $AgNO_3$ is added to $NaAsO_2$ the precipitate first formed is colloidal in nature but at the end-point it settles, leaving a clear supernatant liquid.

When arsenite solutions at different pH values are added to the silver salt, the end-point is marked by a sharp fall in potential (Figs. 1–3). In the reverse process with $AgNO_3$ as titrant, the e.m.f. gradually rises from the beginning of the reaction till at

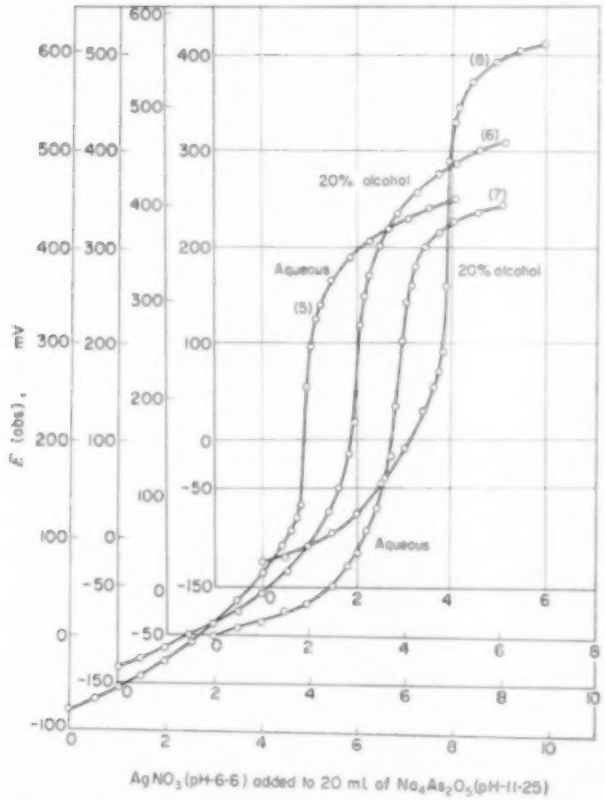



FIG. 5.—Reverse titrations. Curve (5): (M/10)$AgNO_3$; Curve (6): (M/200)$Na_4As_2O_5$; Curve (7): (M/50)$AgNO_3$ and Curve (8): (M/800)$Na_4As_2O_5$.

the equivalence point a marked upward jump is obtained after which the potential assumes an almost constant value (Figs. 4–6). After each addition of the reagent, the e.m.f. rapidly becomes steady; a thorough stirring in the vicinity of the end-point has a favourable effect, and the whole titration takes about half an hour. The titration curves have a regular form; a pronounced maximum in $dE/dC$ is obtained at the end-point and the results are accurate and reproducible. The addition of alcohol to the reaction mixture at varying concentrations slightly improves the end-point, as the presence of alcohol reduces the adsorption of arsenite and also the solubility of silver arsenite precipitates. The arsenite precipitates dissolve in excess of alkali and also in acids and hence the precipitation of one or the other compound depends upon the pH of the medium.

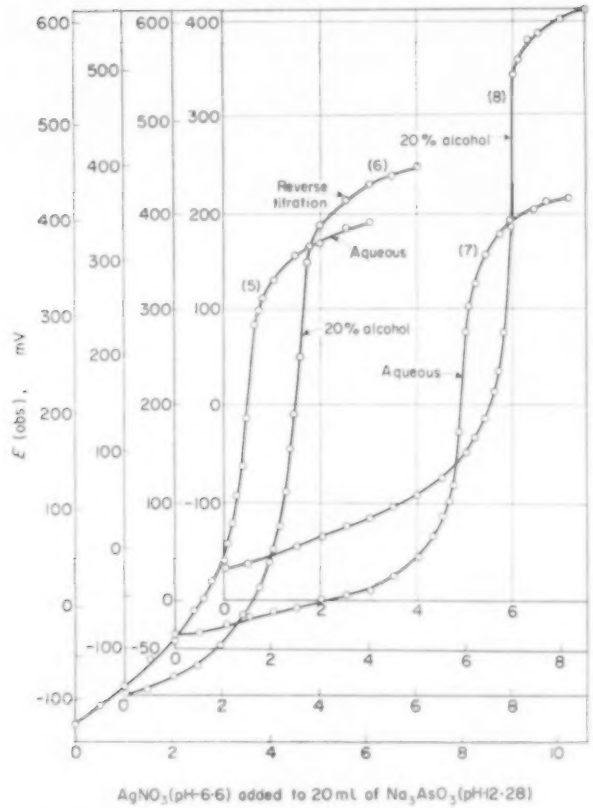



FIG. 6.—Reverse titrations. Curve (5): (M/25)$AgNO_3$; Curve (6): (M/400)$Na_3AsO_3$; Curve (7): (M/10)$AgNO_3$ and Curve (8): (M/100)$Na_3AsO_3$.

The reactions between $AgNO_3$ and $NaAsO_2$ at different pH values can be represented as follows:

$$NaAsO_2 + AgNO_3 = AgAsO_2 + NaNO_3(\text{pH } 9{\cdot}85)$$

$$Na_4As_2O_5 + 4AgNO_3 = Ag_4As_2O_5 + 4NaNO_3(\text{pH } 11{\cdot}25)$$

$$Na_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3NaNO_3(\text{pH } 12{\cdot}28)$$

The composition of silver arsenites can thus be represented by the general formula $x\,Ag_2O{\cdot}As_2O_3$; the proportion of $Ag_2O$ in the compound increases with the amount of alkali used in the preparation of the arsenite solutions i.e., with the pH of the medium

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 45 to 48. Pergamon Press Ltd. Printed in Great Britain.

# SOME REPLACEMENT REACTIONS ON SILICON AND SULPHUR (IV) ATOMS

B. R. CURRELL, M. J. FRAZER, W. GERRARD, E. HAINES and L. LEADER

The Northern Polytechnic, London, N.7

(*Received* 6 *August* 1958; *in final form* 22 *March* 1959)

**Abstract**—Stepwise replacement of the chlorine atoms in silicon tetrachloride by alkoxyl groups has been effected by reaction with dialkyl sulphites. In contrast, there is a slower reaction between tetra-alkoxysilanes and thionyl chloride which leads by successive replacements of alkoxyl groups to silicon tetrachloride. By these reactions it is possible to replace only one chlorine atom in thionyl chloride by an alkoxyl group, and only one alkoxyl group in a dialkyl sulphite by a chlorine atom. These results have correlation with those being obtained in a comprehensive study of mutual replacement of alkoxyl by halogen in inorganic non-metal halide systems.

ol.
12
9/60

THE present work forms part of a more extensive investigation[1,2] into the reactions between esters of inorganic acids and non-metal halides. In general, such reactions yield a mixture of chloro-esters, by mutual replacement reactions on the non-metal atoms. Examples are the fast reaction between alkyl borates and boron trichloride,[3] the catalysed reaction between thionyl chloride and dialkyl sulphites to give the alkyl chlorosulphinate[4] and the much slower reaction between silicon tetrachloride and alkoxysilanes.[5] We are now examining reactions in which the non-metal atoms in the ester and the acid chloride are different.

Successive replacements of the chlorine atoms in silicon tetrachloride with alkoxyl groups has been effected by the action of dialkyl sulphites (equations 1–4). In contrast, tetra-alkoxysilanes react much more slowly with thionyl chloride,

$$SiCl_4 \xrightarrow[(RO)_2SO]{} ROSiCl_3 + ROSOCl \quad (1)$$

$$ROSiCl_3 \xrightarrow[(RO)_2SO]{} (RO)_2SiCl_2 + ROSOCl \quad (2)$$

$$(RO)_2SiCl_2 \xrightarrow[(RO)_2SO]{} (RO)_2SiCl + ROSOCl \quad (3)$$

$$(RO)_2SiCl \xrightarrow[(RO)_2SO]{} (RO)_4Si + ROSOCl \quad (4)$$

although on prolonged treatment it was possible to isolate silicon tetrachloride (equations 5–8). Examination of equations (1)–(8) reveals that,

(1) J. FERTIG, W. GERRARD and H. HERBST, *J. Chem. Soc.* 1488 (1957).
(2) W. GERRARD and J. STRICKSON, *Chem. & Ind.* 860 (1958).
(3) W. GERRARD and M. F. LAPPERT, *J. Chem. Soc.* 2545 (1951).
(4) W. GERRARD, J. PORTER and P. L. WYVILL, *Research* S 33 (1955).
(5) W. GERRARD and J. V. JONES, *J. Chem. Soc.* 1690 (1952).

$$(RO)_4Si \xrightarrow[SOCl_2]{} (RO)_3SiCl + ROSOCl \quad (5)$$

$$\xrightarrow[SOCl_2]{} (RO)_2SiCl_2 + ROSOCl \quad (6)$$

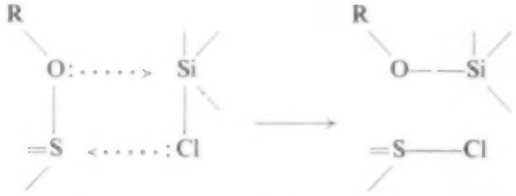
$$\xrightarrow[SOCl_2]{} ROSiCl_3 + ROSOCl \quad (7)$$

$$\xrightarrow[SOCl_2]{} SiCl_4 + ROSOCl \quad (8)$$

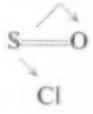
whereas groups attached to silicon are all replaceable this is not the case with the sulphur compounds, and there was no evidence that the chlorosulphinate reacted further with either silicon tetrachloride to give thionyl chloride, or with alkoxysilanes to give dialkyl sulphites.

We believe that a general feature of these reactions is the nucleophilic attack of the alkoxyl oxygen atom of the ester on the non-metal atom of the acid chloride, and also that it may be convenient to consider this process in terms of a "broadside four centre approach."[6]

e.g.




Consequently reactions are encouraged by low electron density on the halide non-metal atom. For example, chlorine attached to silicon facilitates the reaction—(1) is faster than (2), etc.—and the opposite effect is caused by alkoxyl groups, possibly due to back co-ordination from the oxygen to silicon. The inactivity of the chlorosulphinate with silicon chloride and with silicon esters is explained by the weaker nucleophilic power of its oxygen atom, compared with those in the dialkyl sulphites, notwithstanding the expected electrophilic power of sulphur due to:




## EXPERIMENTAL

(1) *Interaction of alkyl sulphites and silicon tetrachloride*

(a) *Sulphite* (4 moles). Silicon tetrachloride (1 mole), the dialkyl sulphite (4 moles) and pyridinium chloride (0·2 g) were heated under reflux at 100° for the time stated (Table 1) until no more sulphur dioxide was evolved. Distillation gave the alkyl chloride and then the tetra-alkoxysilane in the yield stated.

(b) *Sulphite* (3 moles). A mixture of n-butyl sulphite (48·61 g, 3 moles), silicon tetrachloride (1 mole) and pyridinium chloride (0·1 g) was allowed to stand at 20° for 24 hr. Distillation gave n-butyl chloride (83%), b.p. 76–78° and tri-n-butoxychlorosilane (16·5 g, 69%), b.p. 158–163°/10 mm. (Found: Cl, 11·3; Si, 9·4. Calc. for $C_{12}H_{27}O_3ClSi$: Cl, 12·5; Si, 9·9%.)

[6] W. GERRARD, *Chem. & Ind.* 463 (1951).

Vol. 12 1959/6

TABLE 1

| Sulphite | Time (hr) | Tetra-alkoxysilane | | | | | Literature values | |
|---|---|---|---|---|---|---|---|---|
| | | Yield (%) | b.p. | $n_D^{20}$ | Si(%) | | b.p. | $n_D^{20}$ |
| | | | | | Found | Calc. | | |
| Methyl- | 17 | 90 | 118–120° | 1·3705 | 18·4 | 18·3 | 121°[7] | 1·3683[7] |
| Ethyl- | 18 | 86 | 161–166° | 1·3882 | — | — | 68°/18 mm[8] | 1·3840[8] |
| n-Propyl- | 18 | 81 | 106–110°/13 mm | 1·4030 | 10·1 | 10·6 | 73·5°/3 mm[9] | 1·4020[9] |
| Isopropyl- | 30 | 96 | 72–75°/14 mm | 1·3882 | — | — | 74°/13 mm[10] | 1·3835[11] |
| n-Butyl- | 7·5 | 94 | 160–162°/25 mm | 1·4150 | 8·6 | 8·8 | 106–108°/0·5 mm[12] | 1·4139[12] |
| Isobutyl- | 25 | 81 | 127–130°/14 mm | 1·4075 | 8·5 | 8·8 | 90–91°/0·5 mm[12] | 1·4075[13] |
| s-Butyl- | 10 | 85 | 126–128°/20 mm | 1·4100 | 8·6 | 8·8 | 86–88°/0·5 mm[12] | 1·4086[13] |
| n-Octyl- | 24 | 74 | 210°/0·2 mm | 1·4390 | 4·9 | 5·1 | 205–210°/0·5 mm[12] | 1·4396[13] |

(c) *Sulphite* (1 mole). Similarly n-butyl sulphite (24·54 g, 1 mole), silicon tetrachloride (1 mole) and pyridinium chloride (0·5 g) after being at 20° for 24 hr gave n-butoxytrichlorosilane (24·78 g, 94%), redistilled (18·2 g), b.p. 38°/10 mm. (Found: Cl, 50·2; Si, 13·7. Calc. for $C_4H_9OCl_3Si$: Cl, 51·2; Si, 13·5%.)

Mixtures of silicon tetrachloride (1 mole) and dialkyl sulphite (1 mole) were allowed to stand at 20° (a) in the presence and (b) in the absence of pyridinium chloride. After the time intervals shown (Table 2), the unreacted silicon tetrachloride was removed at 15 mm, and the extent of the reaction estimated.

TABLE 2

| Sulphite | (a) Absence of $C_5H_6NCl$ | | (b) Presence of $C_5H_6NCl$ | |
|---|---|---|---|---|
| | Time (hr) | % Reaction | Time (hr) | % Reaction |
| n-Propyl- | 15 | 95·6 | 0·75 | 97·4 |
| Isopropyl- | 1·0 | 77·8 | 1·0 | 96·9 |
| n-Butyl- | 24 | 100·0 | 5·0 | 91·9 |

This catalytic effect has significance, for the frequent use of pyridine for the preparation of esters from inorganic non-metal halides often results in pyridinium chloride being a trace impurity. GERRARD and JONES[5] showed that although pure tetrabutoxysilane and silicon tetrachloride did not react, dialkoxydichlorosilane was slowly formed in the presence of pyridinium chloride. BARTLETT and HERBRANDSON[14] and GERRARD *et al.*[4] have investigated the formation of alkyl chlorosulphinate from thionyl chloride and dialkyl sulphite (equation 9), and have shown that the speed of the reaction is greatly increased by the presence of pyridinium chloride and similar salts, and that this

$$(RO)_2SO + SOCl_2 \xrightarrow{C_5H_5NCl} 2ROSOCl \qquad (9)$$

was not due to the catalysed decomposition of the chlorosulphinate (equation 10).

$$ROSOCl \xrightarrow{C_5H_5NCl} RCl + SO_2 \qquad (10)$$

The necessarily long reaction times in the present work, made the isolation of the alkyl chlorosulphinate product difficult owing to decomposition (equation 10). In fact usually no such attempt was made and the heating was continued until no more sulphur dioxide was evolved. The exact function of the pyridinium chloride in this and other systems is still not clear.


[7] G. FORBES and H. ANDERSON, *J. Amer. Chem. Soc.* **66**, 1703 (1944).
[8] D. F. PEPPARD, W. BROWN and W. JOHNSON, *J. Amer. Chem. Soc.* **68**, 73 (1946).
[9] J. PEAKE *et al.*, *J. Amer. Chem. Soc.* **74**, 1526 (1952).
[10] D. BRADLEY, R. MEHROTRA and W. WARDLAW, *J. Chem. Soc.* 5020 (1952).
[11] T. TAKATANI, *Bull. Chem. Soc. Japan* **27**, 45 (1954).
[12] W. GERRARD and A. WOODHEAD, *J. Chem. Soc.* 519 (1951).
[13] C. MORGAN and W. OLDS, *Industr. Engng. Chem.* **45**, 2592 (1953).
[14] P. D. BARTLETT and H. F. HERBRANDESON, *J. Amer. Chem. Soc.* **74**, 5971 (1952).

(d) *Chlorosulphinate* (1 mole). Silicon tetrachloride (11·04 g, 1 mole) and n-butyl chlorosulphinate (1 mole) were mixed, and after 24 hr at 20°, the unchanged tetrachloride (8·74 g), b.p. 56–58° and n-butyl chlorosulphinate, b.p. 50–52°/2 mm. (Found: Cl, 22·97. Calc. for $C_4H_9O_2ClS$: Cl, 22·66%) were obtained.

n-Butoxytrichlorosilane (11·3 g, 1 mole) and n-butylchlorosulphinate (1 mole) were heated under reflux at 100°/30 mm (12 hr). A liquid (0·5 g) collected in a trap at −80°. Mainly n-butoxytrichlorosilane (11·35 g), b.p. 51–54°/15 mm. (Found: Cl, 43·9. Calc. for $C_4H_9OCl_3Si$: Cl, 51·25%), redistilled b.p. 52°/15 mm. (Found: Cl, 47·7%), a mixture (4·2 g), b.p. 54–65°/15 mm, (Found: Cl, 32·7%), and mainly n-butylchlorosulphinate (2·5 g), b.p. 65–68°/10 mm. (Found: Cl, 24·3. Calc. for $C_4H_9O_2ClS$: Cl, 22·6%) were then isolated.

TABLE 3

| $(RO)_4Si$ | Time (hr) | $SiCl_4$ yield (%) | $(C_{10}H_{10}N_2Cl_4Si)$* (Found: Cl%) |
|---|---|---|---|
| Methoxy- | 17 | 64 | 44·0 |
| Ethoxy- | 25 | 63 | 43·2 |
| n-butoxy- | 42 | 53 | 43·5 |

* Calc. 43·3%

(2) *Interaction of alkoxysilanes and thionyl chloride*

(a) *Thionyl chloride* (4 moles). The tetra-alkoxysilane (1 mole), thionyl chloride (4 moles) and pyridinium chloride (0·8 g) were heated under reflux at 100° for the time stated (Table 3). It was found that separation of the silicon tetrachloride from the reaction mixtures which contained alkyl chloride, thionyl chloride and alkoxychlorosilanes by distillation was protracted; but by addition of excess pyridine in n-pentane, the silicon tetrachloride-pyridine complex[15] was precipitated, filtered, washed, dried and weighed and then the silicon tetrachloride calculated.

(b) *Thionyl chloride* (2 moles). Tetra-n-butoxysilane (32·02 g, 1 mole), thionyl chloride (2 moles) and pyridinium chloride (0·8 g) were heated at 120° for 32 hr. Distillation afforded:

(1) n-butyl chloride (60·5%), b.p. 78° (Found: Cl, 38·5. Calc. for $C_4H_9Cl$: Cl, 38·3%); (2) di-n-butoxydichlorosilane (13·55 g, 56·5%), b.p. 90–104°/17 mm. redistilled (12·3 g) b.p. 102°/18 mm. (Found: Cl, 28·8; Si, 11·32. Calc. for $C_8H_{18}O_2Cl_2Si$: Cl, 28·9; Si, 11·4%) and (3) tri-n-butoxychlorosilane (7·38 g) b.p. 130°/17 mm, redistilled b.p. 134°/18 mm. (Found: Cl, 12·8; Si, 10·4. Calc. for $C_{12}H_{27}O_3ClSi$: Cl, 12·5; Si, 9·9%.)

Tetra-n-butoxysilane (6·4 g, 1 mole) and thionyl chloride (2 mole) in the absence of pyridinium chloride at 100° for 1 hr gave thionyl chloride (3·58 g, 75%), b.p. 60–72°, $n_D^{22}$ 1·5190; impure tri-n-butoxychlorosilane (2·6 g), b.p. 118–140°/10 mm, $n_D^{20}$ 1·4170 and unchanged tetra-n-butoxysilane (3·21 g), b.p. 98°/0·3 mm, $n_D^{20}$ 1·4140 (Found: Si, 8·62. Calc. for $C_{16}H_{36}O_4Si$: Si, 8·76%). In another experiment the same quantities of reactants heated under reflux at 160° for 57 hr gave thionyl chloride (2·66 g, 56%), b.p. 70–73°, $n_D^{23}$ 1·4968; impure tri-n-butoxychlorosilane (4·95 g), b.p. 114–140°/14 mm, $n_D^{22}$ 1·4150 (Found: Cl, 7·03%) and the tetra-ester (0·7 g), b.p. 140°/14 mm, $n_D^{22}$ 1.4140 (Found: Cl, none).

(c) *Thionyl chloride* (1 mole). Thionyl chloride (9·8 g, 1 mole) was added slowly (0·5 hr) to a mixture of tetra-ethoxysilane (1 mole) and pyridinium chloride (0·2 g), at 120°. Distillation gave a fraction (1·10 g), b.p. 45–48°/12 mm, triethoxychlorosilane (13·4 g, 82%), b.p. 52–53°/12 mm. (Found: Cl, 17·5. Calc. for $C_6H_{15}O_3ClSi$: Cl, 17·8%) and a residue (1·90 g).

Tetra-isobutoxysilane (25·90 g, 1 mole), thionyl chloride (1 mole) and pyridinium chloride (0·8 g) heated at 120° for 10 hr gave sulphur dioxide (5·0 g, 0·9 mole), and (1) a liquid (1·7 g), b.p. 60–80°, (2) a fraction consisting of a colourless liquid and some white solid (21·8 g), b.p. 110–120°/15 mm and a residue (1·50 g). Fraction 2 on filtration gave pyridinium chloride (0·75 g) (Found: Cl, 30·2. Calc. for $C_5H_6NCl$: Cl, 30·9%) and a filtrate (20·3 g), which on distillation yielded tri-isobutoxychlorosilane (17·8 g, 79%), b.p. 118–120°/15 mm. (Found: Cl, 12·5. Calc. for $C_{12}H_{27}O_3ClSi$: Cl, 12·5%).

[15] W. R. TROST, *Canad. J. Chem.* **29**, 877 (1951).

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 49 to 59. Pergamon Press Ltd. Printed in Great Britain.

# OBSERVATIONS ON THE RARE EARTHS—LXX*

## SOME CHARACTERISTICS OF ETHYLENEDIAMINETETRAACETIC ACID, N-HYDROXYETHYLETHYLENEDIAMINETRIACETIC ACID, AND 1,2-DIAMINOCYCLOHEXANETETRAACETIC ACID CHELATES OF CERTAIN RARE-EARTH METAL IONS

T. MOELLER and E. P. HORWITZ

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(*Received* 3 *December* 1958)

**Abstract**—Chelates of the types $Ln(HEDTA)\cdot xH_2O$ and $Ba[Ln(DCTA)]_2\cdot yH_2O$ have been isolated for neodymium, samarium, europium, gadolinium and yttrium by precipitation with alcohols. X-ray diffraction data show isomorphism within each series of compounds. Magnetic susceptibility data for several of these chelates and the corresponding ethylenediaminetetraacetate chelates indicate that the 4*f* electrons are not involved in bond formation. Absorption spectra data confirm this conclusion and indicate further that no correlation exists between alterations in absorption characteristics and chelate stability. Infra-red data and dehydration studies suggest that in $Ln(HEDTA)\cdot xH_2O$-type compounds, five co-ordination positions are occupied by the chelating agent and the sixth by water.

THE utility of ethylenediaminetetraacetic acid [abbreviated hereinafter $H_4(EDTA)$] as a complexing agent in ion-exchange separations of both light and heavy rare-earth metal ions has prompted corresponding study of other structurally similar chelating agents, e.g. N-hydroxyethylethylenediaminetriacetic acid [abbreviated $H_3(HEDTA)$] and 1,2-diaminocyclohexanetetraacetic acid [abbreviated $H_4(DCTA)$].[1,2] The interactions in solution of rare-earth metal ions and these three complexing agents have been explored extensively.[1–8]

Although the existence in solution of species of the types Ln(HEDTA) and $Ln(DCTA)^-$ (Ln = yttrium or any rare-earth metal ion) is well established,[1,5] the only description of a corresponding isolated compound is a single observation on the sodium salt of the neodymium-1,2-diaminocyclohexanetetraacetate anion.[8] With ethylenediaminetetraacetate, however, moderately strong acids ($H[Ln(EDTA)(H_2O)]\cdot xH_2O$) and salts ($M^I[Ln(EDTA)(H_2O)]\cdot yH_2O$ and $Ln[Ln(EDTA)(H_2O)]_3\cdot zH_2O$)

* For part LXIX, see T. MOELLER and G. W. CULLEN, *J. Inorg. Nucl. Chem.* **10**, 148 (1959).

(1) F. H. SPEDDING, J. E. POWELL and E. J. WHEELWRIGHT, *J. Amer. Chem. Soc.* **78**, 34 (1956).
(2) L. HOLLECK and L. HARTINGER, *Angew. Chem.* **66**, 586 (1954).
(3) T. MOELLER and J. C. BRANTLEY, *J. Amer. Chem. Soc.* **72**, 5447 (1950).
(4) E. J. WHEELWRIGHT, F. H. SPEDDING and G. SCHWARZENBACH, *J. Amer. Chem. Soc.* **75**, 4196 (1953).
(5) G. SCHWARZENBACH, R. GUT and A. ANDEREGG, *Helv. Chim. Acta* **37**, 937 (1954).
(6) L. HOLLECK and D. ECKARDT, *Z. Naturf.* **8a**, 660 (1953).
(7) L. HOLLECK and D. ECKARDT, *Z. Naturf.* **9a**, 347 (1954).
(8) L. HOLLECK and D. ECKARDT, *Z. Naturf.* **9b**, 274 (1954).

TABLE 1.—ANALYTICAL DATA FOR HEDTA- AND DCTA-CHELATES

| Compound | Ba | | Ln | | C | | N | | H | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| $Y(C_{10}N_2H_{15}O_7)\cdot 6H_2O$ | | | 18·83 | 19·23 | 25·43 | 25·72 | 5·94 | 6·00 | 5·76 | 5·85 |
| $Nd(C_{10}N_2H_{15}O_7)\cdot 6H_2O$ | | | 27·35 | 27·61 | 22·76 | 22·98 | 5·31 | 5·14 | 5·16 | 5·25 |
| $Sm(C_{10}N_2H_{15}O_7)\cdot 5H_2O$ | | | 29·16 | 28·71 | 23·29 | 22·98 | 5·43 | 5·39 | 4·89 | 4·92 |
| $Eu(C_{10}N_2H_{15}O_7)\cdot 5H_2O$ | | | 29·38 | 29·59 | 23·21 | 24·03 | 5·42 | 5·51 | 4·88 | 4·98 |
| $Gd(C_{10}N_2H_{15}O_7)\cdot 6H_2O$ | | | 29·04 | 28·97 | 22·23 | 23·18 | 5·19 | 5·30 | 5·04 | 5·22 |
| $Ba[Y(C_{14}N_2H_{18}O_8)]_2\cdot 13H_2O$ | 11·14 | 10·78 | 14·41 | 14·70 | 27·23 | 28·11 | 4·53 | 4·60 | 5·06 | 5·20 |
| $Ba[Nd(C_{14}N_2H_{18}O_8)]_2\cdot 7H_2O$ | 11·11 | 11·23 | 23·34 | 23·55 | 27·16 | 26·85 | 4·52 | 4·48 | 4·07 | 4·02 |
| $Ba[Sm(C_{14}N_2H_{18}O_8)]_2\cdot 10H_2O$ | 10·54 | 10·76 | 23·10 | 22·82 | 25·78 | 25·51 | 4·30 | 4·23 | 4·32 | 4·29 |
| $Ba[Eu(C_{14}N_2H_{18}O_8)]_2\cdot 9H_2O$ | 10·67 | 11·25 | 23·60 | 24·07 | 26·08 | 27·29 | 4·35 | 4·45 | 4·23 | 4·34 |
| $Ba[Gd(C_{14}N_2H_{18}O_8)]_2\cdot 10H_2O$ | 10·44 | 10·91 | 23·84 | 24·09 | 25·54 | 25·00 | 4·26 | 4·52 | 4·28 | 4·34 |

Vol. 12 1959/60

have been isolated as crystalline solids.[9–14] These compounds have been characterized and related to each other by data from pH titration, X-ray diffraction, differential thermal analysis, and phase rule studies. Infra-red data indicate that no more than five co-ordinating positions of the rare-earth metal ion are occupied by the chelating agent, leaving an uncomplexed carboxyl group.[9]

It was logical, therefore, to extend such studies to the isolation and characterization of HEDTA- and DCTA-type chelates and to apply the techniques of infra-red, visible, and ultra-violet spectra and of magnetic susceptibility to an evaluation of structure and nature of bonding in these species. Some additional data on EDTA-type chelates were obtained for comparison.

## EXPERIMENTAL

*Materials employed.* Yttrium and rare-earth metal oxides of 99+ per cent to atomic weight purity were from the University of Illinois stocks. These were converted to carbonates by dissolving in 25 per cent trichloroacetic acid and hydrolysing on the steam bath to effect precipitation.[15] The crystalline carbonates were removed by suction filtration and dried at 110°C for 48 hr. With praseodymium, the oxide $Pr_6O_{11}$ was reduced with hydrazine hydrate prior to treatment with trichloroacetic acid. Reagent grade ethylenediaminetetraacetic acid, *trans*-1, 2-diaminocyclohexanetetraacetic acid, and N-hydroxyethylethylenediaminetriacetic acid were obtained from the Geigy Chemical Corporation. All other materials were of analytical reagent quality and were used without further purification.

*Preparation of* $Ln(HEDTA)\cdot xH_2O$. Solutions containing the chelates were obtained by treating the yttrium or rare-earth metal carbonate with a hot, aqueous solution of the acid in a 1:1 mole ratio Ln to $H_3(HEDTA)$. In a typical case, 2·0 g ($4{\cdot}28 \times 10^{-3}$ mole) of neodymium carbonate was treated with 2·38 g ($8{\cdot}56 \times 10^{-3}$ mole) of N-hydroxyethylethylenediaminetriacetic acid in 75 ml of water. Reaction to give a clear solution was complete in 10 min.

Evaporation of the resulting solutions yielded tar-like films rather than crystalline products. However, recovery of the chelates was effected by precipitation with i-propanol. In a typical instance, i-propanol was poured slowly and with vigorous shaking into 75 ml of solution containing roughly $8{\cdot}5 \times 10^{-3}$ mole of the neodymium chelate. A finely divided precipitate formed after addition of 200 ml of the alcohol. This precipitate settled in 30 min. The solid was removed, washed with i-propanol, and air-dried for 24 hr. The recovery was 80 per cent. Results with other cations were comparable. The solid chelates are non-hygroscopic powders that dissolve readily in water but not in alcohols or other common organic solvents. They were analysed for carbon, hydrogen and nitrogen by microtechniques and for metal ion by ignition to oxide. Results are summarized in Table 1. The data are consistent with formulation as 1 Ln:1 HEDTA.

Hydrogen analyses suggest that the samarium and europium chelates are 5-hydrates, whereas the neodymium, gadolinium and yttrium compounds are 6-hydrates.

*Preparation of* $Ba[Ln(DCTA)]_2\cdot yH_2O$. Solutions of H[Ln(DCTA)] and Na[Ln(CDTA)] were prepared by treating the carbonates with the free acid in a 0·5:1 mole ratio and the carbonate with acid and sodium hydroxide in a 0·5:1:1 mole ratio, respectively. Both evaporation and the addition of various water-miscible organic liquids yielded tar-like products. However, the barium salts can be precipitated in finely divided, crystalline form by addition of ethanol. In a typical preparation, 2·0 g ($4{\cdot}27 \times 10^{-3}$ mole) of neodymium carbonate and 2·95 g ($8{\cdot}54 \times 10^{-3}$ mole) of 1, 2-diaminocyclohexanetetraacetic acid were stirred together in 100 ml of hot water. Some unreacted acid remained, suggesting the equations

[9] T. Moeller, F. A. J. Moss and R. H. Marshall, *J. Amer. Chem. Soc.* **77**, 3182 (1955).
[10] J. K. Marsh, *J. Chem. Soc.* 1819 (1950); 1461, 3057 (1951); 4804 (1952); 451 (1955).
[11] G. Brunisholz, *Helv. Chim. Acta* **38**, 455, 1654 (1955).
[12] G. Brunisholz, E. Vescovi and M. Lorétan, *Helv. Chim. Acta* **38**, 1186 (1955).
[13] G. Brunisholz and R. Cohen, *Helv. Chim. Acta* **41**, 188 (1958).
[14] G. Brunisholz and M. Randin, *Helv. Chim. Acta* **41**, 195 (1958).
[15] M. L. Salutsky and L. L. Quill, *J. Amer. Chem Soc.* **72**, 3306 (1950).

$$Nd_2(CO_3)_3(s) + 2H_4DCTA \rightarrow 2H[Nd(DCTA)] + 3H_2O + 3CO_2$$

$$Nd_2(CO_3)_3(s) + 6H[Nd(DCTA)] \rightarrow 2Nd[Nd(DCTA)]_3 + 3H_2O + 3CO_2$$

for the process. The resulting filtrate (pH 2) was heated and treated with 0·84 g ($4{\cdot}27 \times 10^{-3}$ mole) of barium carbonate

$$BaCO_3(s) + 2H[Nd(DCTA)] \rightarrow Ba[Nd(DCTA)]_2 + H_2O + CO_2$$

to give a suspension of barium carbonate in a solution (pH 6) of the barium and neodymium salts of the neodymium chelate. Neodymium ions were removed by treating the filtrate with 25 g of Dowex-50 on the barium cycle. The pure barium salt was then precipitated by adding 200 ml of ethanol. The air-dried products are slightly hygroscopic, very soluble in water, and insoluble in alcohols and other common organic solvents. Carbon, hydrogen and nitrogen were determined by micro techniques, barium was determined as sulphate, and yttrium or the rare-earth metal was determined by oxalate precipitation after removal of barium ion. The results are summarized in Table 1. The data are consistent with formulations as 1Ba:2Ln:2DCTA. Hydrogen analyses suggest 10-hydrates for the samarium and gadolinium compounds, but 7-, 9- and 13-hydrates, respectively, for the neodymium, europium and yttrium compounds. Such differences may be due to variations in relative humidity during drying.

*Preparation of* $Na[Ln(EDTA)]\cdot 8H_2O$. The sodium salts of the praseodymium, neodymium, samarium, europium and gadolinium chelates were obtained as previously described.[9] Evaporation gave well-formed crystals in each case.

*X-Ray studies.* Diffraction patterns were obtained with a Norelco Debye–Scherrer type camera with a 114·59 mm diameter, using chromium $K\alpha$ radiation.

*Magnetic susceptibility measurements.* A modified Curie–Chéveneau balance was employed. The balance consists of a torsion arm suspended by a fine wire. One end of the torsion arm supports the sample, which is free to move between the poles of a small permanent magnet so arranged that it can be moved backward or forward with respect to the sample. Movement of the torsion arm is followed by a beam of light reflected on a scale from a mirror attached to the fine wire. Because of its paramagnetic susceptibility, the sample is either repelled or attracted by the magnet and thus automatically aligns in the region of maximum repulsion or attraction. The force acting on the sample is zero both when the sample is exactly centred between the poles and when it is well removed from the poles. Thus, there are two regions wherein the force is maximum as the magnet is moved from far to one side of the sample to far to the other side. In practice, the sample is placed in a small glass tube. The permanent magnet is slowly moved past the sample tube, causing maximum deflexion in one direction. The magnet is then moved back the other way, giving maximum deflexion in the other direction. The difference between the deflexions thus gives the attraction or repulsion from the magnetic field. The magnetic susceptibility is calculated from the relationship

$$\chi = \chi' \frac{m'(\theta - \theta'')}{m(\theta' - \theta'')}$$

where $\chi$ and $m$ are the mass susceptibility and mass of the sample, $\chi'$ and $m'$ have the same connotation for a standard, $\theta$ is the difference in deflexion for the sample, $\theta'$ is the same difference for the standard, and $\theta''$ is the difference for the empty sample tube. The molar susceptibility $\chi_m$ is then determined as

$$\chi_m = \chi M$$

where $M$ is the molecular weight. For the chelates studied, the molecular weights used were those calculated from the analytical compositions. The standard employed was iron(II) ammonium sulphate 6-hydrate, of mass susceptibility $31{\cdot}6 \times 10^{-6}$.[16] The temperature was 27°C.

*Spectrophotometric measurements.* All absorption spectra were measured with a Cary Recording Spectrophotometer Model 14M, using 1 cm quartz cells with water as a reference. The scanning speed was 10 Å/sec.

*Infra-red measurements.* These spectra were obtained with a Perkin–Elmer Model 21 Double Beam Recording Spectrophotometer, using Nujol suspensions between rock salt plates.

*Differential thermal analysis measurements.* These were made with the apparatus of Professor GRIM in the University of Illinois Department of Geology, using calcined alumina as reference.[9]

[16] P. W. SELWOOD, *Magnetochemistry* (2nd Ed.). Interscience, New York (1956).

Vol. 12 1959/6

## RESULTS AND DISCUSSION

The crystallizing propensities of both Ln(HEDTA)·$x$H$_2$O- and Ba[Ln(DCTA)]$_2$·$y$H$_2$O-type compounds are very low. The impossibility of obtaining the materials in other than microcrystalline form by any of the techniques employed is in sharp contrast to easy crystallization of the [Ln(EDTA)]$^-$-type chelates.[9–11] X-ray diffraction patterns inevitably showed much dark background, making it possible to evaluate only a limited number of *d*-spacings from the most intense lines. These are summarized in Table 2. It is apparent from the data recorded that the materials within a given series are isomorphous and that the decrease in spacings with increasing atomic number reflects the lanthanide contraction.

TABLE 2.—X-RAY DIFFRACTION FOR HEDTA- AND DCTA-CHELATES

| Relative intensity* | *d*-spacings (Å) | | | | |
|---|---|---|---|---|---|
| | Y | Nd | Sm | Eu | Gd |
| | | Ln(HEDTA)-Chelates | | | |
| *S* | 9·96 | 10·0 | 10·0 | 9·96 | 9·96 |
| *M* | 8·89 | 8·95 | 8·95 | 8·95 | 8·95 |
| *S* | 8·03 | 8·23 | 8·18 | 8·18 | 8·18 |
| | | Ba[Ln(DCTA)]$_2$-Chelates | | | |
| *Vs* | 14·1 | — | 14·9 | 14·9 | 14·8 |
| *W* | — | — | 11·3 | 11·2 | 11·1 |
| *W* | — | — | 9·39 | 9·39 | 9·26 |
| *M* | — | — | 8·38 | 8·38 | 8·38 |

* *Vs*—very strong, *S*—strong, *M*—medium, *W*—weak.

*Nature of bonding in* Ln(HEDTA)-, Ln(EDTA)$^-$- and Ln(DCTA)$^-$*-type species.* Paramagnetic behaviour among the tripositive rare-earth metal ions is due to the presence of unpaired 4*f* electrons. Since these electrons are well shielded from external influences, both their spin and orbital motions are significant in determining the overall observed susceptibility or moment for an ionic compound. It follows, therefore, that the magnetic moment of a complex containing such a species should indicate clearly whether or not these 4*f* electrons are involved in bond formation. If, as is suggested for EDTA-chelates by absorption spectra measurements,[3,17] bonding does not involve the 4*f* electrons, the magnetic moments of the cations should remain unchanged upon complexing with the polyminepolycarboxylic acid anions in question.

Summarized in Table 3 are values of the moments ($\mu_{eff}$) calculated from the measured susceptibilities in terms of the Curie Law as

$$\mu_{eff} = 2{\cdot}84 \sqrt{(X_m T)}$$

Application of the more rigorous Weiss relationship was precluded by the impossibility of temperature variation with the balance employed. Comparison of these values with those measured for the 8-hydrated sulphates[18] and those calculated

[17] F. A. J. Moss, Doctoral Dissertation, University of Illinois (1952).
[18] D. M. YOST, H. RUSSELL, JR. and C. S. GARNER, *The Rare-Earth Elements and Their Compounds* Chap. 2. John Wiley, New York (1947).

TABLE 3.—MAGNETIC MOMENT DATA FOR HEDTA- AND DCTA-CHELATES

| Ion | $\mu_{eff}$ (Bohr magnetons) | | | | |
|---|---|---|---|---|---|
| | Calc.[19] | $Ln_2(SO_4)_3 \cdot 8H_2O$[18] (min.–max.) | EDTA-Chelate | HEDTA-Chelate | DCTA-Chelate |
| $Pr^{3+}$ | 3·62 | 3·47–3·62 | 3·6 | — | — |
| $Nd^{3+}$ | 3·68 | 3·51–3·62 | 3·6 | 3·3 | 3·5 |
| $Sm^{3+}$ | 1·55–1·65 | 1·32–1·54 | 1·7 | 1·4 | 1·5 |
| $Eu^{3+}$ | 3·40–3·51 | 3·12–3·61 | 3·6 | 3·1 | 3·2 |
| $Gd^{3+}$ | 7·94 | 7·81–8·10 | 7·9 | 7·8 | 8·2 |

for the uncomplexed ions[19] indicates that the 4*f* electrons cannot be of great significance in bond formation in these chelates. It must be emphasized that in evaluating the moments accuracy of measurement did not permit making corrections for underlying diamagnetism in the rare-earth metal ions or for the diamagnetism of the organic ligand or the sodium or barium ion present. Furthermore, the Weiss constant was neglected. However, the Weiss constant is not large when crystals are magnetically dilute, i.e. where the paramagnetic ions do not constitute a large portion of the

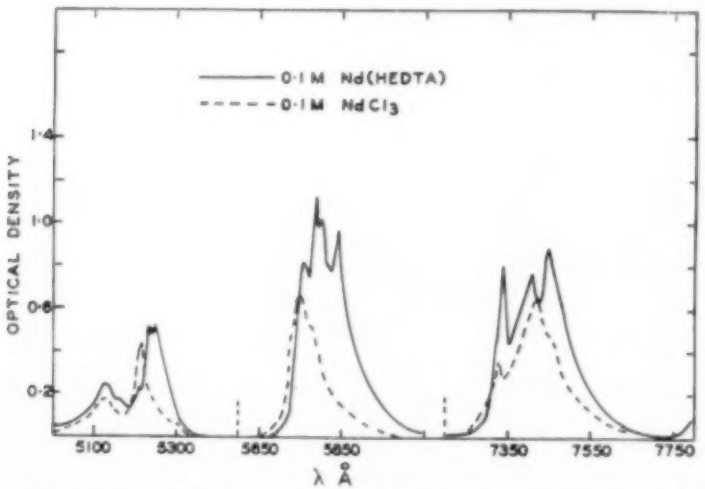



FIG. 1.—Comparison of absorption spectra of neodymium chloride and neodymium-HEDTA chelate.

whole. Such a condition pertains with the chelates in question. The moments given for the gadolinium-containing species are probably the most nearly correct, since the Weiss constant is zero or nearly zero. Agreement here is particularly good.

The sharply defined absorption bands that are characteristic of all the tripositive ions except yttrium, lanthanum and lutetium, whether in solution or in crystalline compounds, are associated with forbidden transitions among the 4*f* orbitals that are

[19] J. H. VAN VLECK and A. FRANK, *Phys. Rev.* **34**, 1494, 1625 (1929).

Vol. 12 1959/6

permitted because of the electric effects of fields imposed by the surrounding anions.[20] The overall spectrum of a given ion, therefore, is altered only in intensities of certain absorption peaks and in resolution of complex bands as the anion environment is altered. Intimacy of association causes the most profound effects with chelating agents.[3,6–8,17,21] These have been described in detail for EDTA-chelates[3,6–8,17] and in lesser detail for certain DCTA-chelates.[6–8] Since a given tripositive ion forms chelates with these structurally analogous species that increase in stability as

$$\text{HEDTA} < \text{EDTA} < \text{DCTA}$$

the possibility of relating observed variations in absorption spectra to chelate stability exists.

Essentially all of the absorption bands in the neodymium spectrum were intensified, shifted to longer wavelengths and resolved into two or more bands of varying sharpness in the presence of the three chelating agents. The spectrum given in Fig. 1 for the Nd-DCTA system is typical. Less pronounced alterations in intensity and wavelengths were observed in the samarium and europium systems. With praseodymium, the major absorption peaks were displaced toward longer wavelengths, but with decreased intensity and no resolution. The observed spectra are described quantitatively by the data in Table 4.

It is significant that regardless of the specific effect of each chelating agent upon individual absorption bands, no new bands in different parts of the spectrum result. This is a further indication that the 4*f* electrons are not involved in bond formation in these chelates. The pronounced alterations noted in the spectra indicate imposition of electrical fields of considerable magnitude. In spite of the expectation that the most strongly chelating group (DCTA) should produce the greatest effect for a given cation, there is no apparent correlation discernible from the data in Table 4. If anything, the largest changes in absorptivity coefficients occur with HEDTA-type materials, which have in turn the smallest formation constants. Similar lack of correlation between alteration in spectrum and complex stability has also been noted in other systems.[21,22]

A possible explanation may lie in the fact that the formation constant is not really a measure of the magnitude of the electric field imposed on the 4*f* electrons. The stability of a complex depends upon the free energy of the complex as a whole in comparison with the free energies of its dissociation products. Both the metal-donor bond energy and the entropy change contribute to the free energy change. Furthermore, the charge on the chelate as a whole may affect the electrical field. Chelates of the HEDTA-type are neutral; the others are anionic.

*Structure of* Ln(HEDTA)-, Ln(EDTA)$^-$- and Ln(DCTA)$^-$*-type species.* Differential thermal analysis of the compound $Ba[Nd(DCTA)]_2 \cdot 7H_2O$ indicated a dehydration step beginning at ca. 50°C and followed by the decomposition of the organic portion of the compound at ca. 200°C. A similar study of the compound $Sm(HEDTA) \cdot 5H_2O$ indicated dehydration beginning at ca. 80°C and decomposition beginning at ca. 250°C.

[20] D. M. Yost, H. Russell, Jr. and C. S. Garner, *The Rare-Earth Elements and Their Compounds* Chap. 3. John Wiley, New York (1947).
[21] R. C. Vickery, *J. Mol. Spectroscopy* **2**, 308 (1958).
[22] R. C. Vickery, *Nature, Lond.* **779**, 626 (1957).

TABLE 4.—ABSORPTION SPECTRA DATA FOR CHLORIDES AND CHELATES

| $Ln^{3+}$ | $LnCl_3$ | | $Ln(EDTA)^-$ | | Ln(HEDTA) | | $Ln(DCTA)^-$ | |
|---|---|---|---|---|---|---|---|---|
| | λ (Å) | a* | λ (Å) | a | λ (Å) | a | λ (Å) | a |
| $Pr^{3+}$ | 4454 | 9·7 | 4450 | 9·6 | 4460 | 9·3 | 4455 | 7·1 |
| | 4690 | 4·2 | 4710 | 4·2 | 4710 | 3·8 | 4710 | 2·9 |
| | 4822 | 3·0 | 4845 | 4·0 | 4845 | 3·7 | 4845 | 2·6 |
| | 5885 | 1·9 | 5890 | 2·1 | 5920 | 1·9 | 5910 | 1·4 |
| $Nd^{3+}$ | 5125 | 1·7 | 5125 | 2·4 | 5140 | 2·3 | 5125 | 1·9 |
| | | | 5170 | 1·6 | 5180 | 1·6 | 5170 | 1·2 |
| | 5218 | 4·3 | 5230 | 5·1 | 5230 | 2·7 | 5235 | 3·7 |
| | | | 5240 | 5·0 | 5250 | 4·4 | 5245 | 3·8 |
| | | | 5250 | 5·1 | 5270 | 4·7 | | |
| | 5745 | 6·7 | 5760 | 8·2 | 5775 | 7·4 | 5760 | 5·5 |
| | | | 5790 | 11·3 | 5810 | 9·9 | 5790 | 6·9 |
| | | | 5800 | 10·2 | 5840 | 9·1 | 5820 | 7·1 |
| | | | 5840 | 9·7 | 5860 | 8·2 | 5840 | 7·6 |
| | 7330 | 3·5 | 7340 | 7·7 | 7390 | 5·8 | 7345 | 7·2 |
| | | | | | | | 7370 | 6·3 |
| | 7420 | 6·6 | 7410 | 7·5 | 7450 | 6·5 | 7410 | 6·2 |
| | | | 7450 | 8·8 | 7525 | 7·2 | 7450 | 6·6 |
| $Sm^{3+}$ | 3445 | 0·54 | 3450 | 1·8 | 3450 | 1·3 | 3450 | 1·8 |
| | 3625 | 0·80 | 3625 | 1·6 | 3630 | 1·1 | 3620 | 1·4 |
| | 3745 | 0·74 | 3750 | 2·0 | 3770 | 1·3 | 3760 | 2·0 |
| | 3910 | 0·27 | 3910 | 0·68 | 3915 | 0·40 | 3910 | 0·48 |
| | 4020 | 3·14 | 4025 | 4·6 | 4030 | 3·6 | 4030 | 3·6 |
| | 4070 | 0·61 | | | | | | |
| | 4150 | 0·46 | 4170 | 1·0 | 4170 | 0·62 | 4170 | 0·72 |
| | 4175 | 0·42 | | | | | | |
| | 4640 | 0·54 | 4630 | 0·80 | 4640 | 0·60 | 4630 | 0·64 |
| | 4790 | 0·57 | 4780 | 1·0 | 4790 | 0·76 | 4770 | 0·64 |
| $Eu^{3+}$ | 3939 | 2·92 | 3945 | 3·4 | 3950 | 3·4 | 3940 | 2·3 |

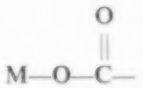
* Absorptivity coefficient = $a = (\log I_0/I)/bc$, where $b$ = depth of cell in cm, $c$ = concentration in mole/l, $I_0$ = intensity of incident light, $I$ = intensity of transmitted light.

Vol. 12 1959/6

Although water of hydration can be removed at relatively low temperature, the strongly exothermic decomposition process follows the endothermic dehydration so closely that complete dehydration before decomposition cannot occur. The EDTA-type compounds behave similarly.[9,17]

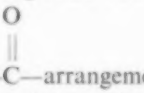
Samples of the compounds Sm(HEDTA)·5$H_2O$ and $NH_4$Sm(EDTA)·8$H_2O$ were dehydrated *in vacuo* over phosphorus(V) oxide for seven days at room temperature. Analyses immediately after removal of the samples from the desiccator showed each to be between a 1-hydrate and a 2-hydrate. Attempted dehydration of the samarium-HEDTA chelate at 111°C over phosphorus(V) oxide resulted in decomposition. A single water molecule thus appears to be held more tenaciously than the others, suggesting that it is within the co-ordination sphere of the cation.

Morris and Busch[23] have postulated that if a carboxyl group is bonded to some metal M as



the carboxylate resonance will increase as the ionic character of the M—O linkage increases. This will in turn impart enhanced single-bond character to the carbonyl group, causing a lowering of the frequency of the C=O stretching frequency. Thus, this frequency should provide some suggestion as to the relative ionic character of the M—O bond. On this basis, it has been shown[23] that one can distinguish between a carboxyl group bonded to a proton and a carboxyl group bonded to a cobalt(III) ion in EDTA-type chelates. It has been shown further[9,23] that if the central metal ion in a chelate forms highly covalent bonds with a carboxyl group, such a carboxyl can be distinguished from an uncomplexed carboxyl group by infra-red measurements.

The infra-red spectra of chelates of the H Ln(EDTA)·$xH_2O$-type show two carbonyl stretching frequencies, one of lesser intensity at 1672 $cm^{-1}$ and another of much greater intensity at 1600 $cm^{-1}$.[9] The former is apparently due to the



—arrangement and the other to carboxyl bonded ionically to the rare-earth metal ion. The relative intensities of the two are consistent with conclusion that the latter is present in the larger quantity and suggest that only five co-ordination positions are satisfied by the EDTA-group.[9] The sixth is assumed to be occupied by a water molecule. With salts of the types M Ln(ETDA)·$yH_2O$ or Ln[Ln(EDTA)]$_3$·$zH_2O$ a single frequency at 1600 $cm^{-1}$ indicates ionic bonding of all four carboxyl groups.

In the HEDTA-type chelates, the enhanced donor ability of the acetate groups over the hydroxyethyl group would suggest that they should bond preferentially to the cation. That this is true is indicated by the presence of but a single broad carbonyl absorption at 1600 $cm^{-1}$, as shown in Fig. 2 for a typical chelate, an absorption characteristic of one kind of carboxyl group. Furthermore, this absorption suggests a high degree of ionic character in the Ln—O bond since the corresponding absorption for the more covalent cobalt(III) material is at 1658 $cm^{-1}$.[23] On the basis of these spectra, it is not possible to determine whether the hydroxyethyl group is co-ordinated.

[23] M. L. Morris and D. H. Busch, *J. Amer. Chem. Soc.* **78**, 5178 (1956).

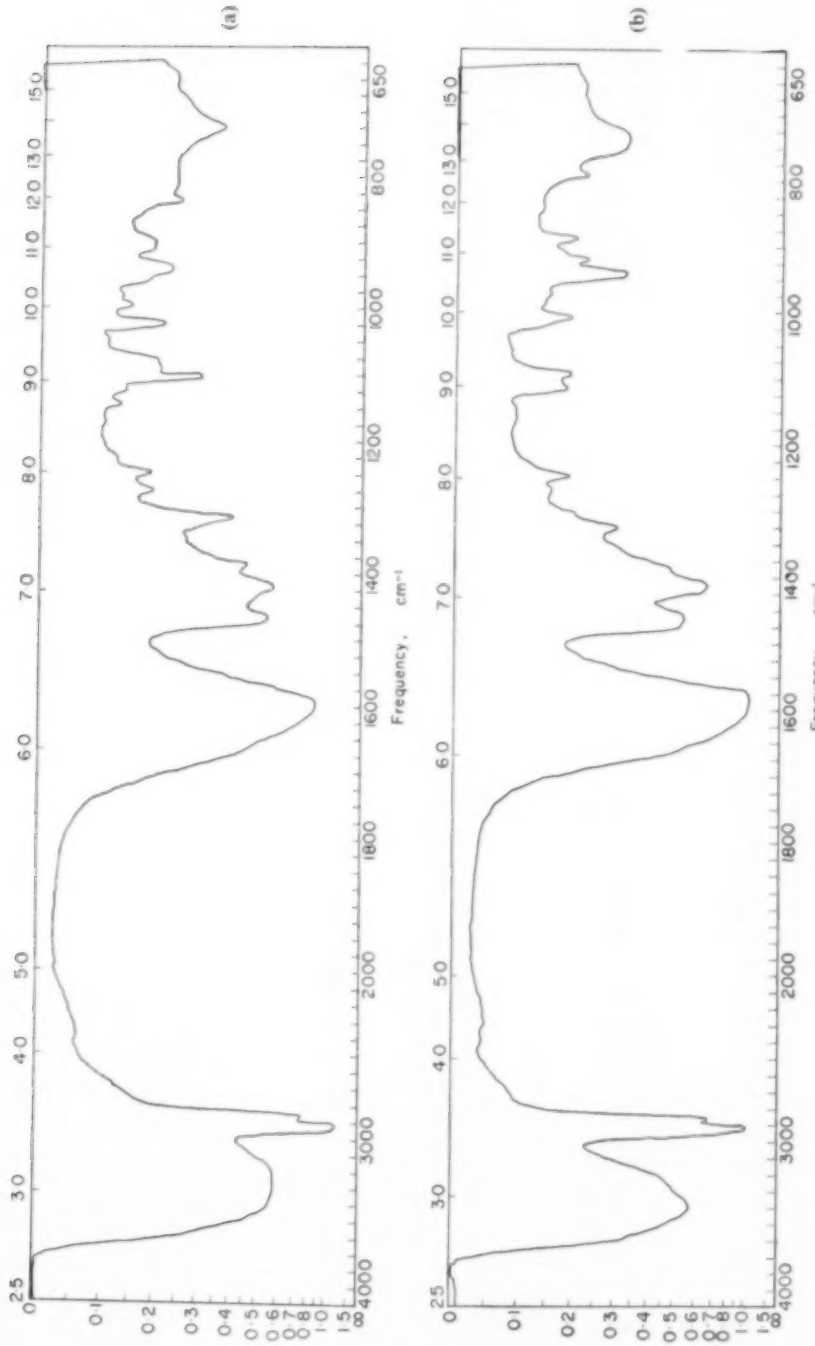



FIG. 2.—Infra-red absorption spectra: (a) $Y(HEDTA)\cdot 6H_2O$; (b) $Ba[Sm(DCTA)]_2\cdot 10H_2O$.

However, the dehydration studies, the generally poor co-ordinating ability of this group, and the striking similarities between the HEDTA- and EDTA-materials all suggest that it is not. Quinquedentate behaviour by the chelating agent with a molecule of water in the co-ordination sphere is therefore reasonable.

The typical infra-red spectrum of a $Ba[Ln(DCTA)]_2 \cdot yH_2O$ compound given in Fig. 2 again shows a single carbonyl frequency centring at 1600 $cm^{-1}$. It is not possible to establish whether the 1,2-diaminocyclohexanetetraacetate ion is acting as a quinquedentate or sexadentate donor because similarities in ionic character between the Ba—O and Ln—O bonds would produce similar displacements in the carbonyl stretching frequency. Unfortunately, it was impossible to prepare a pure compound of the type $H\,Ln(DCTA) \cdot yH_2O$, where distinction between carboxyl groups would be possible. Although dehydration studies suggest strongly the presence of a co-ordinated water molecule in each of the barium salts, it would not necessarily be correct to assume quinquedentate behaviour by analogy to the EDTA-materials since free rotation within the two-carbon bridge between the nitrogen atoms is restricted by the cyclohexane ring structure.

Vol.
12
59/60

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 60 to 70. Pergamon Press Ltd. Printed in Great Britain.

# THE PREPARATION, PHYSICAL PROPERTIES AND INFRA-RED SPECTRA OF SEVERAL NEW ORGANOPHOSPHONATES*

D. F. PEPPARD, J. R. FERRARO and G. W. MASON
Argonne National Laboratory, Box 299, Lemont, Illinois

(*Received* 16 *January* 1959)

**Abstract**—The preparation, physical properties and infra-red spectra of several new organophosphonates [(G′O)GPO(OH)]† are reported. Cryoscopic molecular weights in benzene show that these compounds are dimeric, and infra-red studies of this association in carbon tetrachloride show no free OH absorption in the 3 $\mu$ region. The stronger hydrogen bonding in the organophosphorus compounds of the type $[(GO)_2PO(OH)]$, $[(GO)PO(OH)_2]$, $[GPO(OH)_2]$, [(G′O)GPO(OH)], $[G_2PO(OH)]$ and [GHPO(OH)] as contrasted to the weaker bonding in monocarboxylic acids is discussed.

THE organophosphonic acids of the type $G-PO(OH)_2$ have been reported by KOSOLAPOFF[1] and the physical properties have been investigated fairly extensively. The mono-esters of this acid of the type [(G′O)GPO(OH)] are not as well known. KOSOLAPOFF[1] lists the preparation of several compounds (including phenyl hydrogen phenylphosphonate), but these have not been investigated extensively. RAZUMOV[2] recently reported the preparation of the compound $[(C_2H_5O)C_2H_5PO(OH)]$, and measured its dissociation constant. In view of the excellent solvent extraction properties found for the organophosphoric acids, $(GO)_2PO(OH)$ and $(GO)PO(OH)_2$ and the finding that a direct C—P bond enhances extraction properties of a solvent,[3] i.e. $(G)_3PO > (GO)_3PO$, it was of interest to prepare several new organophosphonates of the type [(G′O)GPO(OH)] for solvent extraction investigations. The solvent properties of this class of compounds will be reported separately. This paper reports the preparation, physical properties and infra-red spectra of several new organophosphonates of the type [(G′O)GPO(OH)]. The system of nomenclature used in this paper corresponds to that suggested by the *Chemical Abstracts* **30**, 4515 (1952).

## PREPARATION OF ORGANOPHOSPHONATE SOLVENTS

Commercial phosphonates, $(G'O)_2GPO$, were used as the starting materials in the preparation of the solvents described in this paper, with the exception of tridecyl hydrogen phenylphosphonate. The neutral phosphonates were hydrolysed with 10 per cent aqueous NaOH (50 per cent excess)

* Based on work performed under the auspices of the U.S. Atomic Energy Commission. Paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in Pittsburgh, Pennsylvania, 1–6 March, 1959.

† G may be an alkyl or aryl group.

(1) G. M. KOSOLAPOFF, *Organophosphorus Compounds*. John Wiley, New York (1950).
(2) A. RAZUMOV and SIM-DO-KHEN, *Zh. Obshchei Khim.* **26**, 2233 (1956).
(3) L. L. BURGER, *Hanford Atomic Products Operation Report*, HW-44888 (1957).



Vol. 12 1959/6

at a temperature of 80° for from 2–48 hr. The aqueous sodium salt solution was scrubbed with benzene to remove any alcohol and unhydrolysed neutral ester. Following acidification, the liberated acidic phosphonate was dissolved in benzene, the benzene solution evaporated, and the organophosphonate freed from any water, alcohol or other volatile materials remaining at reduced pressure. The tridecyl hydrogen phenylphosphonate was obtained from Victor Chemical Works and further purified by the procedure described above.

The elemental analyses for carbon and hydrogen are listed below. Corrections for water content were made. The tri-(n-butyl) phosphate (b.p. 154–157°/10 mm) used as a standard for the elemental analyses was from Eastman Kodak Co.,

Found: H, 10·18; C, 54·12. Calc. for $(C_4H_9O)_3PO$: H, 10·22; C, 54·12.
Found: H, 8·50; C, 62·26. Calc. for $C_8H_{17}OC_6H_5POOH$: H, 8·59; C, 62·27.
Found: H, 11·37; C, 62·65. Calc. for $C_8H_{17}OC_8H_{17}POOH$: H, 11·57; C, 63·00.
Found: H, 5·32; C, 63·73. Calc. for $C_6H_5CH_2OC_6H_5POOH$: H, 5·28; C, 62·96.
Found: H, 9·66; C, 49·38. Calc. for $C_4H_9OC_4H_9POOH$: H, 9·87; C, 49·53.
Found: H, 7·09; C, 56·12. Calc. for $C_4H_9OC_6H_5POOH$: H, 7·07; C, 56·12.
Found: H, 8·46; C, 45·53. Calc. for $C_8H_{17}OClCH_2POOH$: H, 8·31; C, 44·54.
Found: H, 9·73; C, 67·75. Calc. for $C_{13}H_{27}OC_6H_5POOH$: H, 9·78; C, 67·11.

TABLE 1.—PHYSICAL PROPERTIES OF SEVERAL NEW ORGANOPHOSPHONATE SOLVENTS [G′OGPO(OH)]

| Phosphonate solvent | Experimental equivalent weight | Density 20°/20° | Index of refraction 25°C | Viscosity (poises) 20°C | Melting point (°C) | $H_2O$ (%) |
|---|---|---|---|---|---|---|
| 2-Ethylhexyl hydrogen Phenyl | 269 | 1·071 | 1·4974 | 3·916 | — | 0·18 |
| 2-Ethylhexyl hydrogen Benzyl | 305 | 0·956 | 1·4471 | 0·415 | — | nil‡ |
| Phenyl hydrogen n-Butyl | 220 | 1·306† | — | — | 55–57 | 0·30 |
| n-Butyl hydrogen n-Butyl | 192 | 1·024 | 1·4380 | 0·648 | — | 0·39 |
| Phenyl hydrogen Tridecyl* | 211 | 1·150 | 1·5100 | 4·114 | — | 0·21 |
| Phenyl 2-Ethylhexyl hydrogen | 339 | 1·018 | 1·4922 | 4·436 | — | 0·23 |
| Chloromethyl | 241 | 1·111 | 1·4568 | 1·875 | — | nil |

* Tridecyl radical is probably a mixture of several isomeric $C_{13}H_{27}$ radicals with different branching.
† By displacement of mercury.
‡ Less than 0·1 per cent water considered nil.

## PHYSICAL PROPERTIES OF ORGANOPHOSPHONATE SOLVENTS

The equivalent weights of the solvents were obtained by standard alkali titration. Viscosity measurements were made at a constant temperature, controlled at 20 ± 0·025°. Water contents were determined by standard Karl Fischer titration. Table 1 lists the physical properties of these solvents.

*Cryoscopic studies.* Cryoscopic measurements were conducted in a Beckman type freezing-point apparatus using a Beckman differential thermometer. The benzene ("Spectral Grade") and the naphthalene were from Eastman Kodak Co. The acetic acid was obtained from Mallinckrodt Chemical Works (analytical reagent). The method of determination of the freezing-point constants was described previously.[4]

[4] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **7**, 231 (1958).

TABLE 2.—MOLECULAR WEIGHTS OF SEVERAL ORGANOPHOSPHONATES

| Phosphonate solute | Cryoscopic solvent | Molal Conc.* | ΔT (°C) | Experimental (mol. wt.) | Dimeric (mol. wt.) calculated |
|---|---|---|---|---|---|
| 2-Ethylhexyl hydrogen Phenyl [HEH(ϕP)] | Benzene | 0·19 | 0·441 | 591 | |
| | | 0·24 | 0·560 | 596 | 540 |
| | Acetic acid | 0·21 | 0·664 | 300 | |
| 2-Ethylhexyl hydrogen 2-Ethylhexyl [HEH(EHP)] | Naphthalene | 0·12 | 0·429 | 588 | |
| | Benzene | 0·19 | 0·501 | 597 | 610 |
| | Acetic acid | 0·10 | 0·411 | 301 | |
| Benzyl hydrogen Phenyl [HBz(ϕP)] | Naphthalene | 0·14 | 0·403 | 563 | |
| | Benzene | 0·12 | 0·287 | 543 | 496 |
| | Acetic Acid | 0·16 | 0·552 | 281 | |
| n-Butyl hydrogen n-Butyl [HB(BP)] | Benzene | 0·25 | 0·677 | 372 | 388 |
| | Acetic acid | 0·24 | 0·922 | 197 | |
| n-Butyl hydrogen Phenyl [HB(ϕP)] | Benzene | 0·16 | 0·425 | 441 | 428 |
| | Acetic acid | 0·25 | 0·923 | 227 | |
| 2-Ethylhexyl hydrogen Chloromethyl [HEH(ClMP)] | Benzene | 0·19 | 0·433 | 551 | 485 |
| | Acetic acid | 0·16 | 0·538 | 276 | |
| Tridecyl hydrogen Phenyl [HTD(ϕP)] | Benzene | 0·16 | 0·425 | 656 | 612 |
| | Acetic acid | 0·13 | 0·500 | 346 | |
| Phenyl hydrogen† Phenyl [Hϕ(ϕP)] | Benzene | 0·05 | 0·148 | 418 | |
| | | 0·06 | 0·178 | 419 | 468 |
| | Acetic acid | 0·20 | 0·717 | 257 | |

* Molal conc. $= \frac{\text{wt./Formula weight}}{1000\text{ g solvent.}}$

† The limited solubility of this compound in benzene precluded the use of higher concentrations.

The results of the molecular weight determinations for the organophosphonates reported in this paper are shown in Table 2. The abbreviations used in this paper for these compounds are also given in the table.

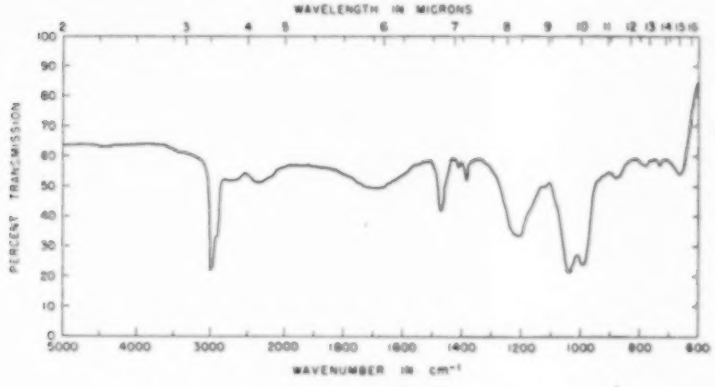
*Absorption measurements.* The infra-red spectra were obtained by means of a Beckman IR-4 spectrophotometer using a sodium chloride prism. Spectral measurements were made on liquid film, KBr disk, or on material dissolved in carbon tetrachloride. The carbon tetrachloride used as a solvent in the spectral determinations was Eastman Kodak Co. "Spectral Grade".

## DISCUSSION AND RESULTS

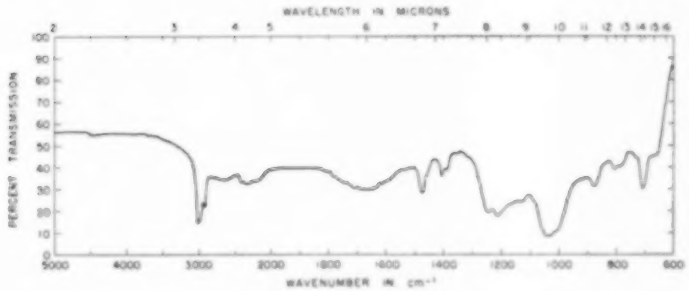
*Cryoscopic studies.* The molecular weights obtained cryoscopically in benzene for the phosphonates studied demonstrate that these substances are dimeric. These acids contain the PO(OH) grouping similar to the monobasic phosphoric acids $[(GO)_2PO(OH)]$[4,5] and the phosphinic acids $[(G)_2PO(OH)]$,[6] which have been

[5] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 371 (1957).
[6] G. M. KOSOLAPOFF and J. S. POWELL, *J. Chem. Soc.* 3535 (1950).

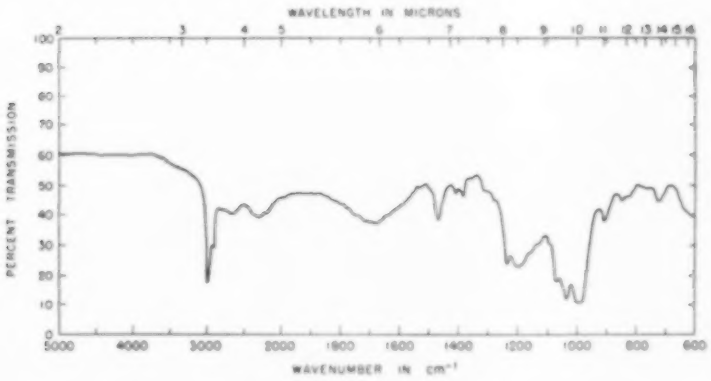
Vol. 12 1959/6




INFRARED ABSORPTION SPECTRUM OF
2-ETHYLHEXYL HYDROGEN 2-ETHYLHEXYLPHOSPHONATE
(Liquid Film)




INFRARED ABSORPTION SPECTRUM OF
2-ETHYLHEXYL HYDROGEN CHLOROMETHYLPHOSPHONATE
(Liquid Film)




INFRARED ABSORPTION SPECTRUM OF
n-BUTYL HYDROGEN n-BUTYLPHOSPHONATE
(Liquid Film)

FIG. 1.—Infra-red spectra of several hydrogen phosphonates from 650–5000 cm$^{-1}$.

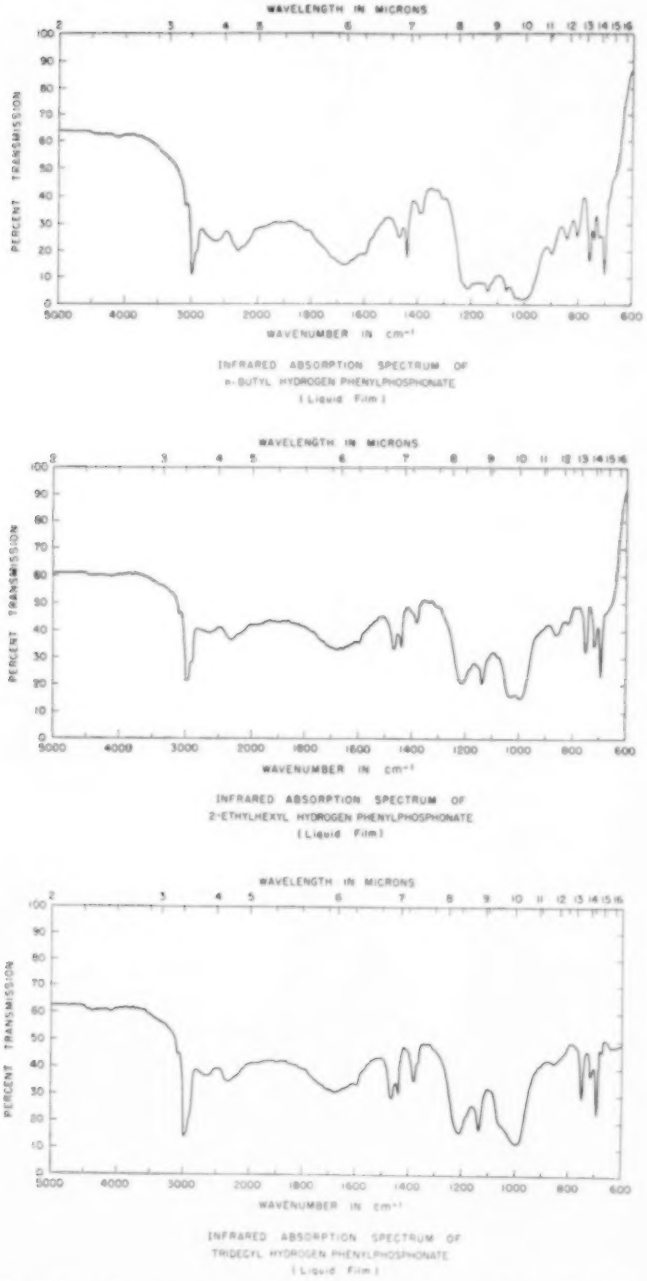
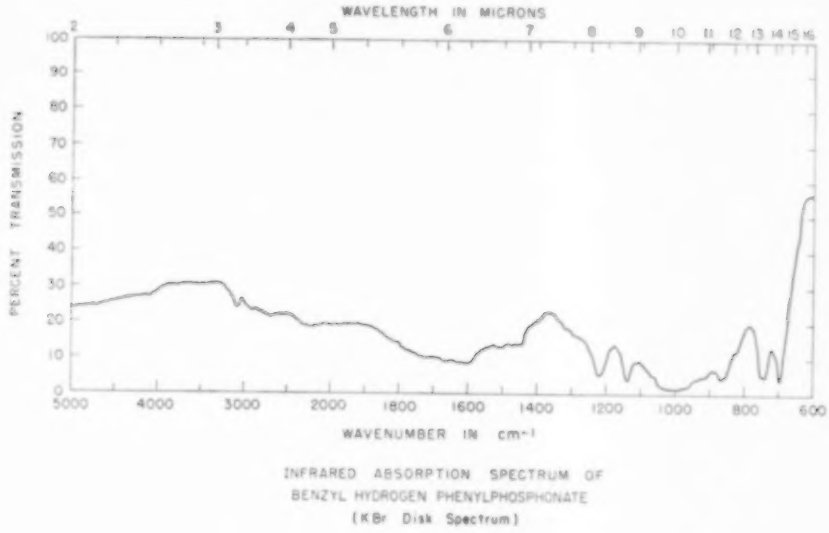
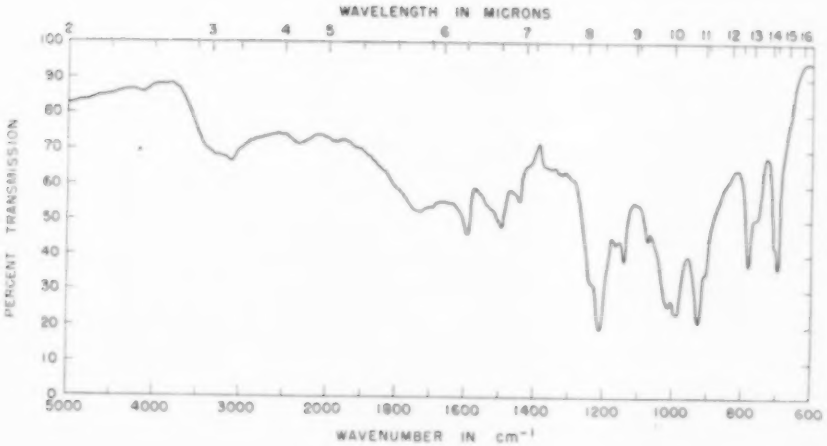



FIG. 2.—Infra-red spectra of several hydrogen phosphonates from 650–5000 $cm^{-1}$

Vol.
12
1959/6




INFRARED ABSORPTION SPECTRUM OF
BENZYL HYDROGEN PHENYLPHOSPHONATE
(KBr Disk Spectrum)




INFRARED ABSORPTION SPECTRUM OF
PHENYL HYDROGEN PHENYLPHOSPHONATE
(KBr Disk Spectrum)

FIG. 3.—Infra-red spectra of several hydrogen phosphonates from 650–5000 $cm^{-1}$

Vol.
12
9/60

reported to be dimeric. The dimers are probably held together through intermolecular hydrogen bonding, stabilization occurring through the formation of an eight-membered ring as has been postulated for the monobasic phosphoric acids.[4,5] In naphthalene, the dimeric state of aggregation is maintained. In acetic acid monomeric molecular weights are obtained, similar to the results obtained for the monobasic and dibasic phosphoric acids.[4] Monomerization has occurred probably through solute–solvent interaction.

*Infra-red studies.* The infra-red spectra from 650–5000 $cm^{-1}$ for the phosphonates are shown in Figs. 1–3. The observed infra-red absorption maxima are listed in Table 3. The spectra all show broad maxima at about 2300 $cm^{-1}$ and 2600 $cm^{-1}$ This is the region postulated as the bonded OH absorption region in organophosphoric acids by BELLAMY,[7,8] and DAASCH and SMITH.[9] The absorption in this region disappears on salt formation. Upon deuteration of the compounds the absorption is shifted to lower frequencies. As a consequence we have assigned the band as the bonded OH stretching absorption band in these phosphonates. Another very broad band is centred at about 1700 $cm^{-1}$ in all these phosphonates. This region also shows a change on deuteration of the compound. The 1700 $cm^{-1}$ region is also present in the monobasic organophosphoric acids.[4] MAARSEN[10] has called the corresponding band in the organophosphoric acids the deformation OH absorption band. It is quite possible that in the phosphonates this band is also due to this absorption.

The absorption in the 1200–1220 $cm^{-1}$ region is due to the P $\rightarrow$ O stretching vibration. The band is broad, and is indicative of a strongly bonded P $\rightarrow$ O group. The P $\rightarrow$ O stretching vibration in the neutral phosphonates of the type $[(G'O)_2GPO]$ is at a higher frequency and is centred in the 1235–1273 $cm^{-1}$ region.[11] The lower frequency value for the acid phosphonates is to be expected because of hydrogen bonding. The results are analogous to those obtained for the monobasic phosphoric acids[4] where the P $\rightarrow$ O stretching vibration is also lower than that observed in the tertiary phosphoric acid esters.

The region at 1440 $cm^{-1}$ seems to be associated with the phenyl group directly bonded to the phosphorus since all the phosphonates having such a phenyl group show this absorption, whereas HB(BP), HEH(EHP) and *bis*-(phenyl) phosphoric acid $[(\phi O)_2PO(OH)]$ do not. This is in agreement with DAASCH's interpretation for the frequency of a $\phi$—P bond.[9] Absorption in the region at 1140 $cm^{-1}$ is also present only in those compounds possessing the phenyl group. The region 1000–1070 $cm^{-1}$ in these phosphonates [G'OG PO(OH)] is the P—O stretching (asymmetric) absorption where G is alkyl. Where G is aryl as in $(\phi O)(\phi)POOH$, the P—O stretching frequency appears at 930 $cm^{-1}$ corresponding to the results of NYQUIST[12] for this absorption in compounds containing the P—O—$\phi$ link. The regions at 2900–3000 $cm^{-1}$ are due to C—H stretching vibrations in the alkyl groups. The absorptions at 3000–3100 $cm^{-1}$ are due to C—H stretching in the aryl groups. The methylene scissoring vibration and the C—H asymmetrical deformation in the alkyl groups are found at about 1470, while the CH symmetrical deformation is at about 1385 $cm^{-1}$. The out-of-plane

(7) L. J. BELLAMY and L. BEECHER, *J. Chem. Soc.* 1701 (1952).
(8) L. J. BELLAMY and L. BEECHER, *J. Chem. Soc.* 728 (1953).
(9) L. W. DAASCH and D. C. SMITH, *Analyt. Chem.* **23**, 853 (1951).
(10) J. W. MAARSEN, M. C. SMIT and J. MATZE, *Rec. Trav. Chim.* **76**, 713 (1957).
(11) L. L. BURGER, *J. Phys. Chem.* **62**, 590 (1958).
(12) R. A. NYQUIST, *J. Appl. Spectroscopy* **4**, 161 (1957).

Vol. 12 1959/6

Vol. 12 9/60



TABLE 3.—ABSORPTION MAXIMA IN $cm^{-1}$ OF SEVERAL ORGANOPHOSPHONATES [G'OGPO(OH)]*

| HB(ΦP) | HEH(ΦP) | HTD(ΦP) | HBz(ΦP) | HΦ(ΦP) | HEH(ClMP) | HB(BP) | HEH(EHP) |
|---|---|---|---|---|---|---|---|
| 3065 (*s*) | 3065 (*s*) | 3065 (*s*) | 3070 (*m*) | 3070 (*w*) | | | |
| 2965 (*sh*) | 2970 (*sh*) | 2956 (*sh*) | | | 2985 (*s*) | | 2975 (*s*) |
| | 2925 (*sh*) | 2925 (*sh*) | | | 2955 (*sh*) | 2970 (*s*) | 2935 (*sh*) |
| 2870 (*sh*) | 2875 (*sh*) | 2880 (*sh*) | | | 2895 (*m*) | 2870 (*sh*) | 2880 (*sh*) |
| 2610 (*m*) *Broad* | 2650 (*m*) *Broad* | 2650 (*m*) *Broad* | 2700 (*m*) *Broad* | | 2650 (*m*) *Broad* | 2650 (*m*) *Broad* | 2700 (*m*) *Broad* |
| | | | | | 2410 (*m*) *Broad* | | |
| 2300 (*m*) *Broad* | 2300 (*m*) *Broad* | 2350 (*m*) *Broad* | 2300 (*m*) *Broad* | 2300 (*w*) *Broad* | 2340 (*m*) *Broad* | 2300 (*m*) *Broad* | 2350 (*m*) *Broad* |
| 1670 (*m*) *Broad* | 1690 (*m*) *Broad* | 1690 (*m*) *Broad* | 1800–1500 (*s*) *Broad* | 1740 (*m*) *Broad* | 1685 (*m*) *Broad* | 1690 (*m*) *Broad* | 1695 (*m*) *Broad* |
| 1595 (*sh*) | 1595 (*sh*) | 1590 (*sh*) | | 1598 (*m*) | | | |
| | | | | 1500 (*m*) | | | |
| 1470 (*w*) | 1468 (*m*) | 1465 (*m*) | 1450 (*m*) | 1445 (*m*) | 1472 (*m*) | 1470 (*m*) | 1470 (*m*) |
| 1440 (*s*) | 1440 (*m*) | 1440 (*m*) | | | 1408 (*w*) | 1410 (*w*) | 1415 (*w*) |
| 1390 (*w*) | 1385 (*m*) | 1380 (*m*) | | | 1385 (*w*) | 1390 (*w*) | 1385 (*m*) |
| | | 1370 (*sh*) | | | | 1318 (*w*) | |
| | | | | 1240 (*sh*) | 1245 (*s*) *Broad* | 1280 (*w*) | |
| 1215 (*s*) *Broad* | 1215 (*s*) *Broad* | 1215 (*s*) *Broad* | 1220 (*m*) | 1215 (*s*) | 1215 (*s*) *Broad* | 1238 (*w*) | 1210 (*s*) *Broad* |
| | | 1190 (*sh*) | | 1170 (*w*) | | 1200 (*m*) | |
| 1140 (*s*) | 1138 (*s*) | 1138 (*s*) | 1145 (*m*) | 1142 (*m*) | | | |
| 1070 (*s*) | 1030 (*s*) | 1080 (*sh*) | | 1078 (*w*) | 1040 (*s*) *Broad* | 1070 (*s*) | 1040 (*s*) |
| 1015 (*s*) | | | 1005 (*s*) *Broad* | | 1010 (*sh*) | 1035 (*s*) | |
| | 995 (*s*) | 998 (*s*) *Broad* | | 995 (*s*) | | 990 (*s*) | 990 (*s*) |
| 900 (*w*) | | | | 928 (*s*) | | 910 (*m*) | |
| 842 (*w*) | 860 (*w*) | 860 (*w*) | 865 (*m*) | | 880 (*w*) | | 883 (*w*) |
| 805 (*w*) | 818 (*w*) | | 820 (*w*) | | 805 (*w*) | 800 (*w*) | |
| 758 (*s*) | 750 (*m*) | 750 (*m*) | 755 (*sh*) | 782 (*m*) | 790 (*w*) | | 780 (*w*) |
| 740 (*w*) | | | 740 (*m*) | 760 (*sh*) | 733 (*w*) | 725 (*w*) | 730 (*w*) |
| 720 (*w*) | 720 (*m*) | 720 (*m*) | 715 (*w*) | 710 (*sh*) | 710 (*m*) | | |
| 700 (*s*) | 695 (*s*) | 695 (*s*) | 700 (*m*) | 698 (*m*) | | | |

* All spectra were made on liquid films with the exception of HBz(ΦP) and HΦ(ΦP), which were KBr disk spectra.

Abbreviations: HB(ΦP) — n-Butyl hydrogen phenylphosphonate
HEH(ΦP) — 2-Ethylhexyl hydrogen phenylphosphonate
HTD(ΦP) — Tridecyl hydrogen phenylphosphonate
HBz(ΦP) — Benzyl hydrogen phenylphosphonate
HΦ(ΦP) — Phenyl hydrogen phenylphosphonate
HEH(ClMP) — 2-Ethylhexyl hydrogen chloromethylphosphonate
HB(BP) — n-Butyl hydrogen n-butylphosphonate
HEH(EHP) — 2-Ethylhexyl hydrogen 2-ethylhexylphosphonate
*sh* — shoulder, *s* — sharp, *m* — medium, *w* — weak.

C—H absorptions for the phenyl ring are found in the region between 690 and 770 $cm^{-1}$ for these compounds.

The infra-red absorption spectra in the 3–4 $\mu$ region of these phosphonates in carbon tetrachloride solution are shown in Fig. 4. The broad 2300–2700 $cm^{-1}$ region appears to be maintained, and no free OH absorption is observed. Similar results were reported for the organophosphoric acids (monobasic and dibasic).[4] Spectra were made on solutions about 0·001 M in $CCl_4$ in large cells (4·5 mm). In these concentrations the monocarboxylic acids show some free hydroxyl absorption, and also some monomeric carbonyl absorption.

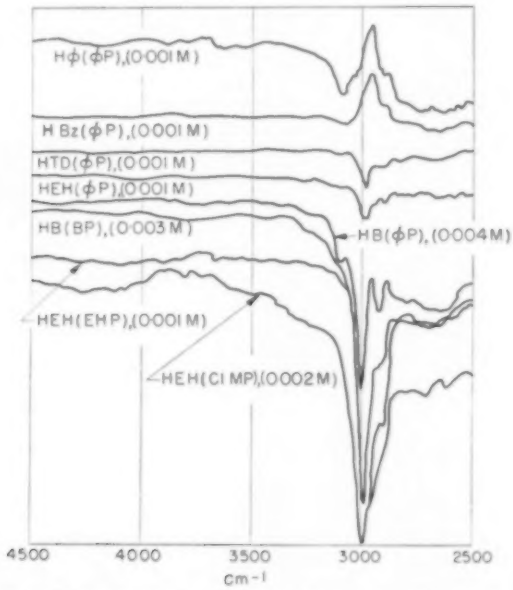



FIG. 4.—Infra-red absorption spectra of several organophosphonates in $CCl_4$ vs. $CCl_4$ [4·5 mm cell] in the OH region.

The infra-red absorption spectra of the phosphonates, (G′O)GPO(OH), in carbon tetrachloride solution in the P → O region are shown in Fig. 5. The P → O stretching stretching frequency shows no change on dilution with $CCl_4$ (~ 0·001 M solutions). The 1200–1220 $cm^{-1}$ region remains broad and indicates that a strongly bonded P ⇀ O exists even in dilute $CCl_4$ solutions.

The relative strength of the hydrogen bond in the dimeric monocarboxylic acids as contrasted to those present in the dimeric substances (monobasic organophosphoric acids, phosphinic acids, and organophosphonates) and the polymeric substances (dibasic organophosphoric acids and phosphonic acids) can be made by a comparison of the cryoscopic molecular weights obtained in various solvents. Table 4 shows the polymerization number obtained for these compounds dissolved in various cryoscopic solvents. It is observed that in benzene the monocarboxylic acids and the organophosphorus acids containing one acidic function [PO(OH)], such as the monobasic organophosphoric acids [$(GO)_2PO(OH)$], and the phosphonates [G′OGPO(OH)] are dimeric. The phosphinic acids [$G_2PO(OH)$], are insoluble in benzene and no

Vol. 12 1959/6

direct comparison can be made. In naphthalene all the acids containing the PO(OH) function are dimeric, whereas benzoic acid has partially depolymerized ($\eta = 1{\cdot}65$). Phenyl phosphinic acid [$\phi$HPO(OH)], appears to be an exception and is capable of associating to a trimer in naphthalene.[6] In camphor, benzoic acid is a monomer, while the phosphorus acids containing the PO(OH) group remain for the most part dimeric. In acetic acid the acids are monomers, probably because of strong solute–solvent interaction. It is concluded that the hydrogen bond is stronger in the acids containing the PO(OH) function than in the monocarboxylic acids.

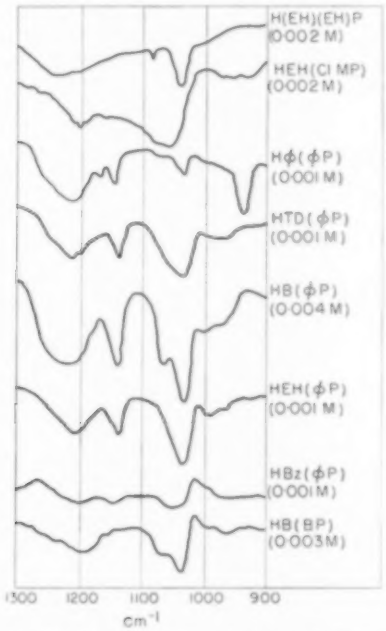



FIG. 5.—Infra-red absorption spectra of several organophosphonates in $CCl_4$ vs. $CCl_4$ [1·5 mm cell] in the P → O region.

The phosphorus acids (dibasic organophosphoric acids and dibasic organophosphonic acids) containing the $PO(OH)_2$ function are polymeric in benzene and in naphthalene, reduce to dimers in camphor and are monomeric in acetic acid. Here, too, it is concluded that the hydrogen bonding is of a stronger nature than in the monocarboxylic acids.

It is of interest to note the stability of the dimeric eight-membered ring in these organophosphorus solvents. In the compounds containing the PO(OH) function the ring is stable in camphor even at 180°. In the compounds containing the $PO(OH)_2$ function the depolymerization in camphor appears to stop at a dimeric state of aggregation. These results seem to indicate that the dimeric eight-membered ring is a basic part of the structure of the dibasic acids and is one of the factors responsible for the stability of the hydrogen bonds found in these organophosphorus solvents.

*Acknowledgements*—The authors wish to thank Dr. J. V. QUAGLIANO of Florida State University, Tallahassee, Florida, for his critical review of the infra-red portion of this work, and Miss IRENE FOX of Argonne National Laboratory for the elemental analyses.

TABLE 4.—POLYMERIZATION NUMBER* $\eta$ OF SEVERAL ORGANOPHOSPHORUS SOLVENTS IN VARIOUS CRYOSCOPIC SOLVENTS

| Solute | Cryoscopic solvents | | | |
|---|---|---|---|---|
| Monocarboxylic acids | Benzene | Naphthalene | Acetic acid | *d*-camphor |
| Benzoic acid | 1·96 | 1·65 | 1·00 | 1·0 |
| Monobasic organophosphoric acids $[(GO)_2PO(OH)]$ | | | | |
| HDEHP | 1·94 | 1·99 | 1·06 | 1·9 |
| HD(O$\Phi$)P | 2·00 | 2·03 | 1·06 | 1·9 |
| HD($\beta$-N)P | insol. | 2·02 | insol. | 1·8 |
| HD(p-T)P | 2·22 | — | 1·14 | 1·7 |
| HD$\Phi$P | 2·50 | 2·48 | 1·19 | 2·0 |
| Dibasic organophosphoric acids $[(GO)PO(OH)_2]$ | | | | |
| $H_2$MEHP | 6·35 | 6·12 | 1·00 | 1·9 |
| $H_2$M(O$\Phi$)P | (gels) | 8·16 | 1·05 | 2·0 |
| Organophosphonic acids $[(G\text{-}PO(OH)_2]$ | | | | |
| $C_6H_5PO(OH)_2$ | insol. | insol.† | 1·06[13] | 2·4 |
| Hydrogen phosphonates $[GOG'PO(OH)]$ | | | | |
| HBz($\Phi$P) | 2·19 | 2·27 | 1·16 | 1·6 |
| HEH(EHP) | 1·95 | 1·92 | 0·98 | 1·8 |
| Organophosphinic acids $[G_2PO(OH)]$ | | | | |
| G-PO(OH) / H | | | | |
| $(C_6H_5)_2PO(OH)$ | insol. | 2·33 | 1·00[13] | — |
| $\Phi$-PO(OH) / H | insol. | 2·70 | 1·03[13] | 1·8 |

* Polymerization Number $= \dfrac{\text{apparent molecular weight}}{\text{formula weight}} = \eta$

† Other compounds of this class found to be hexameric in naphthalene.[7]

Abbreviations:

HDEHP — Bis-(2-ethylhexyl)-phosphoric acid
HD(O$\Phi$)P — Bis-[p-(1,1,3,3-tetramethylbutyl)-phenyl]-phosphoric acid
HD($\beta$-N) — Bis-($\beta$-naphthyl)-phosphoric acid
HD(p-T)P — Bis-(p-tolyl)-phosphoric acid
HD$\Phi$P — Bis-(phenyl)-phosphoric acid
$H_2$MEHP — Mono-(2-ethylhexyl)-phosphoric acid
$H_2$M(O$\Phi$)P — Mono-[p-(1,1,3,3-tetramethylbutyl)-phenyl]-phosphoric acid

[13] L. D. FREEDMAN and G. O. DOAK, *J. Org. Chem.* **21**, 1533 (1956).

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 71 to 78. Pergamon Press Ltd. Printed in Great Britain.

# SEXAVALENT COMPOUNDS OF URANIUM—I

## URANYL ALKOXIDES AND URANIUM HEXA-ALKOXIDES.

D. C. BRADLEY, AMAR K. CHATTERJEE and AMIYA K. CHATTERJEE
Birkbeck College, Malet Street, London, W.C.1

(*Received* 23 *February* 1959)

**Abstract**—The preparation of uranyl alkoxides was complicated by either the insoluble nature of these compounds or their tendency to disproportionate. Insoluble uranyl methoxide, $UO_2(OMe)_2$, MeOH was obtained from the reaction involving uranyl chloride and methanolic lithium methoxide. Uranyl ethoxide $UO_2(OEt)_2$, 2EtOH was obtained similarly. Uranyl iso-amyloxide was obtained by the action of iso-amyl alcohol and ammonia on either uranyl chloride or dipyridinium uranyl chloride. The action of various alcohols on uranyl methoxide was studied and in some cases (mainly secondary and tertiary alcohols) a remarkable disproportionation occurred with the ultimate formation of uranium hexa-alkoxide $U(OR)_6$. Some properties of the hexa-alkoxides are described. The hexa-t-butoxide is remarkably resistant to hydrolysis.

ol.
12
9/60

A STRIKING feature of the chemistry of sexavalent uranium is the existence of many compounds containing the $UO_2$ group. However, a survey of the literature[1] reveals few cases in which structures of uranyl compounds have been determined and there is still doubt as to the structure of the $UO_2$ group itself.[2] In view of recent structural work on the metal alkoxides[3] it seemed worthwhile to prepare and study uranyl alkoxides. Only two references to uranyl alkoxides could be found in the literature. ALBERS *et al.*[4] obtained uranyl iso-amyloxide as a red solid soluble in hydrocarbon solvents by the reaction between uranyl chloride and sodium iso-amyloxide in iso-amyl alcohol. Recently, JONES *et al.*[5] described two interesting uranyl alkoxides. One was a brown crystalline solvated ethoxide $UO_2(OEt)_2$, 3EtOH, obtained from the reaction involving uranyl chloride and sodium ethoxide, in which the three molecules of co-ordinated alcohol resisted the action of heat at 200°C under 0·004 mm pressure. This is very surprising and we have not succeeded in repeating this work. Their second compound, provisionally assigned the formula $UO_2(OBu^t)_2$, $4Bu^tOH$, was obtained as red crystals from uranium (IV) tetra-t-butoxide, either by the action of heat *in vacuo* or by treatment with oxygen in petroleum ether solution.

In a preliminary communication[6] we reported that the preparation of uranyl alkoxides by reactions involving alcoholic solutions of uranyl chloride with either ammonia or the appropriate sodium alkoxide was complicated by the insoluble nature

[1] A. E. COMYNS, AERE/C/R 2320 (1957).
[2] L. SACCONI, G. CAROTI and P. PAOLETTI, *J. Chem. Soc.* 4257 (1958).
[3] D. C. BRADLEY, *Nature, Lond.* **182**, 1211 (1958).
[4] H. ALBERS, M. DEUTSCH, W. KRASTINAT and H. VON OSTEN, *Ber. Dtsch. Chem. Ges.* **85**, 267 (1952).
[5] R. G. JONES, E. BINDSCHADLER, G. A. MARTIN, J. R. THIRTLE and H. GILMAN, *J. Amer. Chem. Soc.* **79**, 4921 (1957).
[6] D. C. BRADLEY, AMAR K. CHATTERJEE and AMIYA K. CHATTERJEE, *Proc. Chem. Soc.* 260 (1957).

of some of the uranyl alkoxides or their tendency to disproportionate. Nevertheless, due to the high solubility of lithium chloride in methanol we prepared the very sparingly soluble uranyl methoxide by means of the following reaction:

$$UO_2Cl_2 + 2LiOMe + MeOH \longrightarrow UO_2(OMe)_2,\ MeOH \downarrow + 2LiCl$$

The disproportionation of uranyl alkoxides in alcoholic solution with the ultimate formation of some hexa-alkoxide must involve the splitting of the $UO_2$ group under very mild conditions. To our knowledge this process was without precedent in uranium chemistry and required further investigation. We now report the results of the action of various alcohols on uranyl methoxide and of the preparation of some new uranyl alkoxides and uranium hexa-alkoxides.

*Reactions involving uranyl methoxide and primary alcohols*

When uranyl methoxide was treated with either ethyl, n-propyl or isobutyl alcohols, methyl alcohol was liberated and the sparingly soluble crystalline uranyl alkoxide was formed. The amount of disproportionation accompanying these alcohol interchanges was very small. Similarly, iso-amyl alcohol caused interchange to a soluble uranyl iso-amyloxide. This is important because it rules out the possibility that straightforward interchange is confined to alcohols which produce insoluble uranyl alkoxides.

*Reactions involving uranyl methoxide and secondary or tertiary alcohols*

When uranyl methoxide was treated with either isopropyl, s-butyl or t-butyl alcohols the interchange was accompanied by disproportionation. In each case the solution assumed a deep blood-red colour and an insoluble residue was formed. From the solution a deep red crystalline solid was obtained with the composition close to that of $UO(OR)_4$, ROH and which gave, when heated *in vacuo*, the volatile hexa-alkoxide and an insoluble non-volatile residue. These reactions were repeated several times in order to establish this unique disproportionation reaction beyond doubt and, although the precise compositions of the intermediate products varied slightly from one preparation tc another, the general pattern of the reaction was constant and some hexa-alkoxide was always formed. It must be emphasised that even a small amount of *hydrolysis* would have a very marked effect on the composition and proportions of the intermediate products of the disproportionation. Nevertheless, we were able to establish, by means of a careful uranium and alkoxide balance between starting material and products, that the reaction involved was a true disproportionation. For example, in one of the reactions involving isopropyl alcohol the products agreed reasonably with the requirements of the following equations:

(a) Solvolytic disproportionation:

$$3UO_2(OPr^i)_2,\ Pr^iOH \longrightarrow U_2O_5(OPr^i)_2,\ 2Pr^iOH \downarrow + UO(OPr^i)_4,\ Pr^iOH$$

(b) Thermal disproportionation:

$$5UO(OPr^i)_4,\ Pr^iOH \longrightarrow U_2O_5(OPr^i)_2,\ 2Pr^iOH + 3U(OPr^i)_6 \uparrow + 3Pr^iOH \uparrow$$

On the other hand, when uranyl methoxide was treated with t-amyl alcohol, no disproportionation occurred, and uranyl t-amyloxide $UO_2(OAm^t)_2$ was isolated as a solid which was soluble in t-amyl alcohol but insoluble in benzene. This was most

Vol 12 1959/

interesting because it might have been suggested that the presence of secondary or tertiary-alkyl groups was essential for the disproportionation process to occur. This may yet be true because it is possible that steric factors may prevent the disproportionation when tertiary amyloxide groups are involved.

*Uranium hexa-alkoxides*

Uranium hexa-isopropoxide was first described by JONES *et al.*[7] who also prepared the hexa-ethoxide, -methoxide and -n-propoxide. Their molecular weight determination on the hexa-ethoxide in benzene (cryoscopic method) indicated a degree of polymerization (i.e. ratio of observed mol. wt. : mol. wt. of monomer) of ca. 1·2 which suggests a significant proportion of dimer species. The hexa-s-butoxide and hexa-t-butoxide obtained in this work are now reported for the first time although the latter was first obtained independently by one of us[8] in an attempted preparation of uranium (V) penta-t-butoxide by alcoholysis of the penta-ethoxide. We have determined the volatilities and molecular weights of the hexa-alkoxides: $U(OR)_6$ where R = $Pr^i$, $Bu^s$ and $Bu^t$, and the results are given in Table 1.

TABLE 1

| R in $U(OR)_6$ | Volatility at 0·01 mm | Mol. wt. | Degree of polymerization |
|---|---|---|---|
| Isopropyl | 65° | 656 | 1·1 |
| s-Butyl | 75° | 680 | 1·0 |
| t-Butyl | 85° | 680 | 1·0 |

Vol. 12 59/60

The molecular weights were determined ebullioscopically in benzene and it is interesting to note that although the s-butoxide and t-butoxide are monomeric the isopropoxide contains a small proportion of dimer (cf. ethoxide). From the structural viewpoint it has been predicted[3] that uranium in a hexa-alkoxide can achieve the eight-co-ordinated state in the dimer $U_2(OR)_{12}$ but it is clear that such a structure would be very sensitive to steric factors. We hope to obtain more conclusive evidence on this matter in future studies on uranium hexa-methoxide. It was surprising to find the hexa-t-butoxide less volatile than the s-butoxide but it must be remembered that the temperatures recorded above are not equilibrium boiling points but sublimation points.

*Uranyl ethoxide*

The uranyl ethoxide obtained by ethanolysis of uranyl methoxide was a light brown powder with a composition near to $UO_2(OEt)_2$, 2EtOH. It lost the addended alcohol at 80°/0·05 mm in contrast to the compound described by JONES *et al.* (*loc cit.*) which retained its ethanol even at 200° *in vacuo*. We repeated the reaction described by JONES *et al.* but obtained no uranyl ethoxide. On the other hand, treatment of ethanolic uranyl chloride with lithium ethoxide followed by exhaustive

[7] R. G. JONES, E. BINDSCHADLER, D. BLUME, G. KARMAS, G. A. MARTIN, J. R. THIRTLE, F. A. YEOMAN and H. GILMAN, *J. Amer. Chem. Soc.* **78**, 6030 (1956).
[8] D. C. BRADLEY. Unpublished work.

extraction of the precipitate with ethanol to remove lithium chloride left uranyl ethoxide similar in composition to that obtained by ethanolysis of uranyl methoxide. Moreover, aerial oxidation of ethanolic uranium (V) penta-ethoxide caused the deposition of crystalline $UO_2(OEt)_2$, 2EtOH and we are convinced that this is the proper composition of uranyl ethoxide. Unfortunately the very low solubility of the compound in either ethanol or benzene precluded a molecular weight determination. It is noteworthy that uranyl chloride also formed a di-ethylalcoholate $UO_2Cl_2$, 2EtOH. This compound was sparingly soluble in benzene while in boiling ethanol it was practically monomeric.

*Uranyl isoamlyoxide*

When uranyl methoxide was treated with a boiling iso-amyl alcohol-benzene mixture the uranium compound slowly dissolved and from the red solution the uranyl isoamyloxide was isolated as a brown solid with a composition near to $UO_2(OAm^f)_2$, $Am^fOH$. The anhydrous compound, obtained by heating the solvate at 78°/0·05 mm, was insoluble in benzene. The solvate was also isolated from reactions involving either uranyl chloride or pyridinium uranyl chloride with iso-amyl alcohol and ammonia:

$$(C_5H_6N)_2UO_2Cl_4 + 3Am^fOH + 4NH_3 \longrightarrow UO_2(OAm^f)_2, Am^fOH + 4NH_4Cl + 2C_5H_5N$$

$$UO_2Cl_2 + 3Am^fOH + 2NH_3 \longrightarrow UO_2(OAm^f)_2, Am^fOH + 2NH_4Cl.$$

*Structural aspects of uranyl alkoxides*

It is unfortunate that all of the uranyl alkoxides obtained in this work were too insoluble to permit molecular weight determinations. However, it is noteworthy that the solvated uranyl ethoxide $UO_2(OEt)_2$, 2EtOH, in which each uranium atom is presumably linked to at least six oxygens, should be insoluble. We should expect a monomeric unit containing six-co-ordinated uranium to be soluble and it therefore seems probable that the uranium is here exhibiting a higher co-ordination number (e.g. eight). In the latter case the *smallest* possible polymer should be a trimer (assuming the -OEt and HOEt groups to be disposed roughly octahedrally around the $UO_2$ groups), although infinite linear polymers could not be ruled out. With uranyl methoxide $UO_2(OMe)_2$, MeOH similar arguments would predict an octamer as the *smallest* possible polymer for eight-co-ordinated uranium whilst an alternative configuration involving a two-dimensional infinite sheet polymer is feasible. Therefore, it is reasonable to suppose that the low solubility of uranyl alkoxides is due to the polymeric nature of these compounds which results from the eight-co-ordination of the uranium by oxygen.

## EXPERIMENTAL

Uranyl alkoxides are very readily hydrolysed and special precautions were taken throughout this work to exclude moisture by means of the techniques already described in our earlier work.[9,10]

[9] D. C. BRADLEY, B. N. CHAKRAVARTI and A. K. CHATTERJEE, *J. Inorg. Nucl. Chem.* **3**, 367 (1957).
[10] D. C. BRADLEY and A. K. CHATTERJEE, *J. Inorg. Nucl. Chem.* **4**, 279 (1957).

Vol. 12 1959/6

*Analytical methods*

(i) *Uranium.* When chloride was present, the uranium in nitric acid solution was precipitated in carbonate-free conditions as ammonium diuranate. The precipitate was filtered off, washed with ammoniacal 2 per cent ammonium nitrate solution and carefully ignited and the uranium determined as $U_3O_8$. The filtrate was acidified with nitric acid and the chloride determined gravimetrically as AgCl. When no chloride was present the sample was weighed into a platinum crucible and hydrolysed with water. The residue, left after evaporating off the volatile products under an infra-red lamp, was dissolved in a few drops of nitric acid (d. 1·42), the solution was then evaporated to dryness and the uranyl nitrate was ignited to $U_3O_8$.

(ii) *Alkoxide.* The ethoxide and isopropoxide determinations were carried out volumetrically by the chromic acid method already described.[9] Methoxide was determined similarly but with the following modification to ensure complete oxidation to carbon dioxide: the mixture of sample and chromic acid was kept in a closed vessel for 2 hr at room temperature and then boiled under reflux for about 10 min. The excess chromic acid in the cooled solution was then determined iodometrically in the usual way.

*Pyridinium uranyl chloride*

Uranyl chloride hydrate (20 g) was dissolved in ethanol (325 ml) and the solution was saturated with hydrogen chloride. Pyridine (17 g) was added and, on treatment with more hydrogen chloride, the pale yellow-green complex chloride (28·5 g) crystallized out. (Found: U, 41·5; Cl, 24·8. Calc. for $(C_5H_6N)_2UO_2Cl_4$; U, 41·6; Cl, 24·8%.)

*Anhydrous uranyl chloride*

Although various methods are available for preparing anhydrous uranyl chloride, we found difficulty in obtaining the pure material. Following a considerable amount of research we found that the pure compound could be obtained from the hydrated chloride as follows: the powdered hydrate in a silica boat was heated in a stream of anhydrous hydrogen chloride for several hours at 300°. The solid was next ground up under dry nitrogen and then heated at 400° in a mixture of hydrogen chloride and chlorine for a further 2–3 hr. (Found: U, 69·8; Cl, 20·6. Calc. for $UO_2Cl_2$; U, 69·8; Cl, 20·8%.)

*Uranyl chloride ethyl alcoholate*

Uranyl chloride hydrate (23·1 g) was dissolved in a mixture of ethanol (300 ml) and benzene (130 ml) and the solution was carefully fractionated to remove the water as the ternary azeotrope water–ethanol–benzene. When the solution had become concentrated to 250 ml more benzene (50 ml) was added and the fractionation continued. When all of the benzene had been removed, the alcoholic solution was concentrated under reduced pressure but the product would not crystallize. Finally, the solution was taken to dryness at room temperature under low pressure (0·1 mm) and gave a pale yellow solid (25·4 g). (Found: U, 54·7; Cl, 16·0; EtO, 20·4. Calc. for $UO_2Cl_2$, 2EtOH: U, 54·9; Cl, 16·4; EtO, 20·8%.) In boiling ethanol the *alcoholate* has a molecular weight of 421 (Calc. for $UO_2Cl_2$, 2EtOH: 433). It was practically insoluble in benzene.

*Uranyl methoxide*

Uranyl chloride (anhydrous, 16·6 g) was dissolved in methanol (200 ml) in the boiler flask of a Soxhlet extractor. Lithium (0·67 g) was placed in a sintered glass (porosity No. 2) extraction thimble in the Soxhlet and allowed to react with methanol condensing from the boiling solution of uranyl chloride. The lithium methoxide solution was then siphoned over automatically into the uranyl chloride solution. This was continued until all of the lithium had dissolved. The suspension of uranyl methoxide was heated for a further 27 hr and then allowed to cool and settle. The methanolic lithium chloride solution was then decanted off and the uranyl methoxide was washed several times by decantation with anhydrous methanol (50 ml portions). After drying at room temperature under low pressure (0·1 mm), the uranyl methoxide was left as a bright yellow microcrystalline solid. (Found: U, 65·0; MeO, 24·0. Calc. for $UO_2(OMe)_2$, MeOH: U, 65·4; MeO, 25·5%.) A sample of the foregoing product heated at 100°/0·05 mm for 3 hr slowly changed colour to brown and lost the majority of its addended alcohol. (Found: U, 68·3; MeO, 18·6. Calc. for $UO_2(OMe)_2$: U, 71·7; MeO, 18·7%.)

*Uranyl ethoxide*

(i) *From uranyl methoxide.* Ethanol (179 g) and benzene (88 g) were added to uranyl methoxide (10 g) and the mixture was subjected to fractional distillation to remove the methanol–benzene azeotrope. The colour of the solution became wine-red but little solid appeared to dissolve. When the interchange was judged complete, the mother liquor was decanted off and the buff-coloured uranyl ethoxide (11·9 g) was dried at room temperature under 0·1 mm pressure. (Found: U, 53·5; EtO, 37·5. Calc. for $UO(_2OEt)_2$, 2EtOH: U, 52·7; EtO, 39·8%.) The mother liquor was evaporated to dryness and left only a trace of red liquid which from its volatility was doubtless uranium hexaethoxide. A sample or uranyl ethoxide heated at 80°/0·05 mm for 4 hr lost its addended ethanol. (Found: U, 66·7; EtO, 23·1. Calc. for $UO_2(OEt)_2$: U, 66·1; EtO, 25·0%.)

(ii) *From uranyl chloride.* Anhydrous uranyl chloride (6·8 g) in boiling ethanol (200 ml) was caused to react with lithium ethoxide obtained from lithium (0·28 g) in the Soxhlet extractor. The sparingly soluble uranyl ethoxide was obtained as a buff-coloured solid (6·3 g) after being washed several times with ethanol by decantation and dried at room temperature under 0·1 mm pressure. (Found: U, 52·1; EtO, 36·1; Cl, 1·0%.) A sample heated at 100°/0·05 mm for 5 hr changed to a brick-red colour and had obviously decomposed. (Found: U, 68·5; EtO, 20·5; ratio EtO:U, 1·58.) In view of the fact that uranyl ethoxide obtained in this work lost its addended ethanol at 80° *in vacuo* and began decomposing at 100°, we were surprised by the behaviour reported by JONES *et al.*[5] for a compound $UO_2(OEt)_2$, 3EtOH. They claimed that this compound was obtained by allowing sodium ethoxide to react with ethanolic uranyl chloride followed by evaporation of the solvent, heating the residue to 200°/0·005 mm and extracting it with ether. Their product was obtained from the ether extract. From a reaction involving uranyl chloride (10·2 g) and sodium ethoxide (from Na, 1·30 g), carried out under closely similar conditions, we obtained a black residue which was completely insoluble in ether and which had an analysis near to that of the expected mixture of uranium trioxide and sodium chloride. (Found: U, 59·2. Calc. for mixture of $UO_3$ + 2NaCl: U, 59·1%.)

*Uranyl isopropoxide*

(i) *Reaction involving pyridinium uranyl chloride.* The complex chloride (13 g) suspended in a mixture of isopropanol (119 g) and benzene (129 g) was treated with excess ammonia and an exothermic reaction occurred. After filtration, evaporation of the filtrate left a red-brown substance (0·84 g). (Found: U, 45·6; $Pr^iO$, 11·4; Cl, 15·5%; Ratio $Pr^iO$:U, 1·01; Cl:U, 2·27.) The precipitate of impure ammonium chloride (15·2 g) evidently contained the major proportion of the uranium. (Found U, 37·4; $Pr^iO$, 18·2; Cl, 22·3; $NH_2$, 13·5%.)

(ii) *Reaction involving sodium isopropoxide and uranyl chloride.* Uranyl chloride hydrate (8·2 g) was azeotropically dehydrated in benzene–isopropanol solution, the benzene removed by fractionation and the isopropanolic solution treated with sodium isopropoxide formed from sodium (0·90 g) in a Soxhlet apparatus. The precipitate was filtered off and the filtrate evaporated to dryness under 0·1 mm pressure left a red-brown solid (3 g). (Found: U, 43·1; $Pr^iO$, 52·1; Cl, 2·1%. Ratio $Pr^iO$:U, 4·75; Cl:U, 0·33.) A sample (2 g) of the foregoing product was refluxed with isopropanol (93 g) and on cooling some crystals (0·52 g) were formed. (Found: U, 51·5; $Pr^iO$, 38·7. Calc. for $UO_2(OPr^i)_2$, $Pr^iOH$: U, 53·1; $Pr^iO$, 39·5%.) This experiment is typical of several carried out with these reactants.

(iii) *Isopropanolysis of uranyl iso-amyloxide.* Uranyl iso-amyloxide (2·6 g) was treated with increasing quantities of boiling isopropanol until 110 ml had been added. However, some insoluble material still remained and the cooled wine-red solution was filtered and the filtrate taken to dryness under 0·1 mm pressure leaving a deep red solid (0·5 g). (Found: U, 45·7; $Pr^iO$, 56·5. Calc. for $UO(OPr^i)_4$, $Pr^iOH$: U, 43·3; $Pr^iO$, 53·6%.) The insoluble fraction appeared to be a hydrolysis product. (Found: U, 67·9; $Pr^iO$, 23·2%. Ratio $Pr^iO$:U, 1·37). In the light of subsequent work it is clear that disproportionation of the uranyl isopropoxide must have occurred in this reaction.

(iv) *Isopropanolysis of uranyl methoxide.* When uranyl methoxide $UO_2(OMe)_2$, MeOH was treated with isopropanol, methanol was fractionated off but the solution became red and the insoluble uranium compound became brown. From the filtrate a red solid (near to $UO(OPr^i)_4$, $Pr^iOH$ in composition) was isolated and this gave uranium hexa-isopropoxide when heated *in vacuo*. Some typical results are given in Table 2 for the solvolytic disproportionation.

In Table 3 some results are presented for the thermal disproportionation at 110°/0·05 mm of the soluble fractions (B).

Vol. 12 1959/6

To establish the presence of "active hydrogen" (i.e. isopropanol) in the soluble fraction (B), a sample (0·421 g) from experiment (iv) (Table 2) was treated with methyl magnesium iodide in di-n-butyl ether and the methane (20·61 ml at s.t.p.) collected in a gas burette. (Found: Active H, 0·225. Calc. for $UO(OPr^i)_4$, $Pr^iOH$: Active H, 0·184%.) This determination does not necessarily distinguish between $UO(OPr^i)_4$, $Pr^iOH$ and $U(OH)(OPr^i)_5$. A portion of the sublimed uranium hexa-isopropoxide obtained in experiment (iii) (Table 3) was heated in a molecular still at 0·01 mm and it began to sublime at 65°. Sublimation was rapid at 85° and no residue remained.

TABLE 2

| Wt. of $UO_2(OMe)_2$, MeOH taken (g) | Wt. of $Pr^iOH$ (g) | Insoluble residue A | | | Soluble product B | | |
|---|---|---|---|---|---|---|---|
| | | Wt. (g) | Composition (%) | | Wt. (g) | Composition (%) | |
| | | | U | $Pr^iO$ | | U | $Pr^iO$ |
| (i) 6·72 | 301·5 | 3·66 | 63·4 | 22·8 | 4·07 | 49·5 | 43·3 |
| (ii) 7·01 | 193·8 | 4·79 | 60·1 | 27·5 | 2·01 | 42·4 | 53·9 |
| (iii) 12·08 | 261·4 | 9·04 | — | — | 3·24 | 43·2 | 51·5 |
| (iv) 11·76 | 236·0 | 10·02 | 63·3 | 27·9 | 3·64 | 41·7 | 55·8 |

*Uranyl n-propoxide*

Uranyl methoxide (11·1 g) was treated with boiling n-propanol (400 ml) until no more methanol could be collected by fractionation. Not all of the solid dissolved and the solution became red and, on cooling, deposited crystals. Some of the crystals were separated from the main solid residue by flotation in the mother liquor from which they were finally separated by filtration. The crystalline n-propoxide (0·5 g) was cream-coloured. (Found: U, 61·3. Calc. for $UO_2(OPr^i)_2$: U, 61·3%.) The mother liquor was evaporated to dryness leaving a small amount of viscous red product which, at 120–125°/0·05 mm, gave a drop of red condensate. There was insufficient of the latter for analysis but from its appearance and volatility it was undoubtedly uranium hexa-n-propoxide. The main solid product (13·6 g) was extracted with boiling n-propanol and gave a second crop of crystalline uranyl n-propoxide which was separated from undissolved product by flotation. (Found: U, 62·0%.)

TABLE 3

| Wt. of (B) taken (g) | Non-volatile residue | | | Sublimate | | | $U(OPr^i)_6$ requires | |
|---|---|---|---|---|---|---|---|---|
| | Wt. (g) | Composition (%) | | Wt. (g) | Composition (%) | | U (%) | $Pr^iO$ (%) |
| | | U | $Pr^iO$ | | U | $Pr^iO$ | | |
| (i) 3·0 | 2·2 | 63·3 | 29·1 | 0·402 | 40·1 | 60·1 | 40·2 | 59·8 |
| (ii) 1·85 | — | — | — | 1·04 | 40·1 | 60·1 | 40·2 | 59·8 |
| (iii) 2·70 | — | — | — | 1·30 | 40·2 | 60·0 | 40·2 | 59·8 |

*Uranyl isobutoxide*

The reaction involving isobutanol and uranyl methoxide resembled that involving n-propanol. A sparingly soluble crystalline solvated uranyl isobutoxide was obtained. (Found: U, 48·5. Calc. for $UO_2(OBu^i)_2$, $Bu^iOH$: U, 48·6%.)

*Uranyl iso-amyloxide*

(i) *From pyridinium uranyl chloride.* The complex chloride (11·1 g) suspended in isoamyl alcohol–benzene azeotrope (200 ml) was treated with ammonia until the exothermic reaction was complete. After the removal of ammonium chloride the wine-red filtrate was evaporated under 0·1 mm pressure and left a brown solid (6·8 g). (Found: U, 44·8. Calc. for $UO_2(OAm^i)_2$, $Am^iOH$: U, 44·7%.)

(ii) *From uranyl chloride hydrate.* The hydrate (5·0 g) was azeotropically dehydrated using isoamyl alcohol (25 ml), benzene (75 ml) and isopropanol (5 ml). The latter served to effect the removal

of water as the ternary azeotrope of benzene-isopropanol-water. Then the remainder of the isopropanol was removed as the binary azeotrope with benzene leaving a benzene-iso-amyl alcohol solution of uranyl chloride iso-amyl alcoholate. The latter was treated with excess ammonia and, after filtering off the ammonium chloride, uranyl isoamyloxide alcoholate (2·6 g) was obtained by evaporation of the filtrate. (Found: U, 44·1%.) The co-ordinated isoamyl alcohol was removed by heating at 75°/0·05 mm. (Found: U, 53·6%. Calc. for $UO_2(OAm^i)_2$: U, 53·6%.)

(iii) *From uranyl methoxide.* Uranyl methoxide (9·5 g) slowly dissolved when treated with boiling iso-amyl alcohol–benzene azeotrope (275 ml) and gave a clear red solution. Evaporation of the solvent under 0·1 mm pressure left uranyl iso-amyloxide solvate (12·8 g). (Found: U, 46·2%.)

TABLE 4

| R in $U(OR)_6$ | Range of wts. of solute (g) | Wt. of $C_6H_6$ | Slope ($\Delta T°/g$) | Mol. wt. | |
|---|---|---|---|---|---|
| | | | | Found | Calc. |
| Isopropyl | 0·0288–0·2098 | 15·93 | 0·280 | 656 | 592 |
| s-Butyl | 0·0110–0·0406 | 15·63 | 0·276 | 680 | 676 |
| t-Butyl | 0·0321–0·1581 | 14·77 | 0·296 | 680 | 676 |

*Uranyl t-amyloxide*

Uranyl methoxide (8·09 g) was interchanged with t-amyl alcohol (300 ml) giving a brown solution and a small amount (1·2 g) of insoluble residue. (Found: U, 62·0%.) From the mother liquor, evaporated to dryness, a deep maroon crystalline product (8·36 g) was obtained. (Found: U, 54·2; C, 23·3; H, 4·51. Calc. for $UO_2(OAm^t)_2$: U, 53·6; C, 27·2; H, 4·95%.) The product gave no volatile fraction when heated to 120°/0·05 mm and at 135° it turned black due to decomposition. (Found: U, 72·9%.)

*Disproportionation of uranyl t-butoxide*

When uranyl methoxide was treated with t-butanol–benzene azeotrope, alcohol interchange was accompanied by disproportionation. One experiment using uranyl methoxide (10·34 g) and t-butanol–benzene azeotrope (250 ml) gave an insoluble residue (8·09 g) and a soluble red crystalline solid (3·74 g). (Found: U, 38·6; C, 38·7; H, 7·48. Calc. for $UO(OBu^t)_4$, $Bu^tOH$: U, 38·4; C, 38·7; H, 7·40%.) The latter (2·3 g) heated at 110°/0·05 mm in a molecular still gave a deep red sublimate of uranium hexa-t-butoxide (0·267 g, Found: U, 34·7; C, 42·2; H, 8·05. Calc. for $U(OBu^t)_6$: U, 35·2; C, 42·6; H, 7·90%.) The hexa-t-butoxide, in a molecular still, began to sublime at 85°/0·04 mm and sublimed rapidly at 110° leaving no residue. Compared with metal alkoxides in general, uranium hexa-t-butoxide is remarkably resistant to hydrolysis, apparently remaining unaffected by exposure to the air. A benzene solution of the hexa-t-butoxide could be shaken with water for some time before hydrolysis occurred. In aqueous acetone solution the compound was slowly hydrolysed to uranium trioxide. The resistance to hydrolysis is undoubtedly due to the strong shielding of the uranium by six t-butoxide groups preventing nucleophilic attack by water molecules.

*Disproportionation of uranyl s-butoxide*

The reaction involving uranyl methoxide and s-butanol closely paralleled that involving t-butanol. From the methoxide (11·4 g) and s-butanol–benzene azeotrope (350 ml) an insoluble brown fraction (7·98 g, Found: U, 62·5%) and a soluble red compound (5·82 g, Found: U, 40·3%) were obtained. A sample (4·83 g) of the latter heated in a molecular still gave at 110–125°/0·05 mm a deep red sublimate (0·84 g, Found: U, 35·1. Calc. for $U(OBu^t)_6$: U, 35·2%) of the hexa-s-butoxide and a non-volatile residue (Found: U, 53·0%). The hexa-s-butoxide began to sublime at 75°/0·01 mm in a molecular still and sublimed rapidly and completely at 110°.

*Molecular weights of uranium hexa-alkoxides*

The molecular weights were determined ebullioscopically in benzene using the previously described[10] all-glass ebulliometer. The compounds showed no variation of molecular weight with concentration over the range studied. The results are given in Table 4.

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 79 to 83. Pergamon Press Ltd. Printed in Great Britain.

# SOME STUDIES ON TUNGSTIC ACID PREPARED BY ION EXCHANGE

E. RICHARDSON
Whitehaven College of Further Education, Whitehaven, Cumberland, England

(*Received* 26 *January* 1959)

**Abstract**—A method is described for the preparation of tungstic acid by ion exchange. The acid prepared is unstable and decomposes to form white tungstic acid. Breaks occur in the conductometric and potentiometric titration curves of the acid at Na:W ratios of 1:2 and 2:1; the acid is not, however, metatungstic acid but is probably a hexatungstic acid $H_2[H_2W_6O_{21}]$. The influence of polyhydroxy compounds on the conductivity of this acid has been studied.

THREE forms of tungstic acid are described in the literature,[1] a yellow form of empirical formula $H_2WO_4$, precipitated by addition of mineral acid to a hot solution of either normal or paratungstate and a white form with the composition $WO_3 \cdot xH_2O$ precipitated by acidification of cold tungstate solutions. White tungstic acid is said to give an acid reaction to indicators, to have a strong tendency to become colloidal, and to decompose if warmed to form the yellow variety. Metatungstic acid, the third form, is obtained by acidifications of soluble metatungstates which are prepared from boiling acidified solutions of alkali tungstates. The free acid is soluble in water but may be extracted from solution with ether, with which it forms an insoluble complex.

It was felt of interest to investigate the nature of tungstic acid prepared by ion exchange. Molybdic acid prepared by this technique is different in form from other molybdic acids described in the literature and separates from solution as a colourless transparent glass.[2]

## EXPERIMENTAL

AnalaR sodium tungstate dihydrate, $Na_2WO_4 \cdot 2H_2O$, was used in most of the experiments; this salt is readily soluble in cold water. In some experiments sparingly soluble ammonium tungstate was used; sufficient dissolves on boiling to form an 0·1 M solution (with respect to $WO_3$). This solution was cooled before exchange.

Zeokarb 225, a sulphonated polystyrene resin, was used in the hydrogen form in all studies. The resin was conditioned before use by alternate washings with 2 N NaOH, water and 2 N HCl. Excess acid was removed from the column after the final regeneration by washing with distilled water until the conductivity of the washings collected was less than 3 $\mu$mhos. It was found most convenient to prepare the acid in small quantities when required, using a small column, since the acid is unstable; moreover, the use of a large column in many cases led to deposition of colloidal material within the resin.

All conductivity measurements were made using a Mullard conductivity bridge operating in the most sensitive range with a dip type cell of constant 1·459. All pH measurements were made using a Cambridge pH meter with a glass-calomel electrode system calibrated by buffer solutions complying with modern standards.

All experiments were conducted at 18°C unless otherwise specified.

[1] H. REMY, *Treatise on Inorganic Chemistry* Vol. 2. Elsevier, New York (1956).
[2] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **9**, 267 (1959).

## RESULTS AND DISCUSSION

### 1. *Properties of tungstic acid prepared by ion exchange*

The solution obtained from the column was clear to the eye and varied in colour from a very pale yellow (0·01 M $WO_3$) to a deep yellow (0·35 M $WO_3$). The solution obtained from 0·1 M $Na_2WO_4$ became turbid within an hour although no precipitate was visible to the naked eye. On standing overnight, however, a copious white precipitate was formed. This precipitate gradually changed colour and after 2–3 days became a pale yellow. If the solution is diluted to 0·0075 M immediately after preparation no turbidity appears during the first day and a yellow precipitate only appears

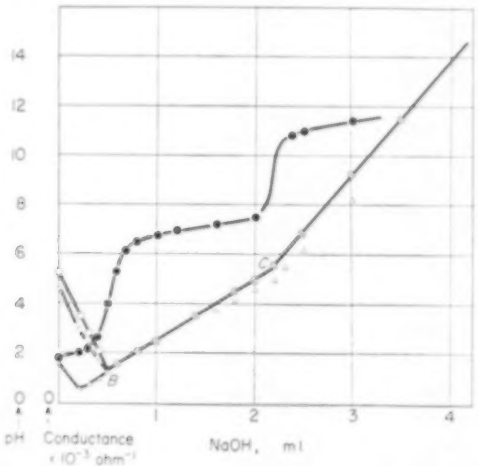



FIG. 1.—Conductometric and potentiometric titration of tungstic acid.
Conductance × $10^{-3}$ $\Omega^{-1}$ against ml N NaOH.
● = pH Titration.
○ = Immediate conductometric titration.
× = Conductometric titration after standing 3 hr.
△ = Conductometric titration after standing 5 days.
Note: ○ and × are co-incident after *B*.
△ is co-incident with ○ and × from *B* to where shown.

after standing 3–5 days. The most concentrated solution prepared (0·35 M $WO_3$) which was a clear yellow immediately after preparation, became extremely viscous within 1 hr and gelled within 3 hr.

Potentiometric and conductometric titration curves obtained by titrating this tungstic acid solution with N NaOH are shown in Fig. 1. Curves with breaks at similar Na : W ratios were also obtained from more concentrated and from more dilute solutions. The breaks which occur in both potentiometric and conductometric curves correspond to Na : W ratios of 1 : 2 and 2 : 1. The former break corresponds to the replacement of the hydrogen ion of a strong acid, the latter to the conversion of the soluble tungstic acid present to $Na_2WO_4$.

The soluble tungstic acid concentration determined by titration, however, does not agree with the total tungsten content determined gravimetrically by precipitation as the oxinate, after boiling with a suitable buffer solution. The gravimetric result

was always some 15 per cent greater than that obtained by titration. It is evident, therefore, that not all of the tungsten is present in solution as simple acid. It is fortunate, however, that the excess tungsten present, presumably in colloidal form, is only slowly attacked by sodium hydroxide during the time taken for a conductometric titration, and does not interfere appreciably in the determination of the nature of the free acid except in concentrated solution. For comparison, it may be noted that silica sols, clear to the naked eye, contain colloidal material unreactive to ammonium molybdate, which decomposes slowly in sodium hydroxide solution.[3]

Conductometric titration curves are included in Fig. 1 for the same quantity of tungstic acid titrated immediately after preparation, after standing 3 hr and after standing 5 days before titration. Although the solution had a definite white turbidity and the conductance had decreased from $0{\cdot}53 \times 10^{-2}$ to $0{\cdot}47 \times 10^{-2}\ \Omega^{-1}$ after standing 3 hr, little difference was apparent in the shape of the conductometric titration curves.

In a further experiment two samples of tungstic acid were made M and 0·1 M with respect to potassium chloride. An immediate white precipitate was obtained from the molar solution; in the 0·1 M solution no precipitate was observed but the solution became faintly white and turbid. Potentiometric titration of this solution gave a curve identical in shape with Fig. 1. The turbidity disappeared at a Na : W ratio of 1 : 1.

From these experiments it appears that the available acid hydrogen of the slightly turbid solution is similar to that of the freshly prepared one. The colloidal acid formed at this stage of the aggregation process must therefore have a labile structure in which hydrogen can readily be replaced by sodium.

Vol. 12 59/60

In some experiments sparingly soluble ammonium tungstate was used in place of sodium tungstate. Passage of a 0·01 M solution of ammonium tungstate through the resin in every case produced a turbid solution (immediately after preparation) which obviously contained much colloidal material.

From the Na : W ratios at the breaks in the titration curves shown in Fig. 1 it is obvious that the acid cannot be a soluble form of either white tungstic acid (formulated by most authors as $H_2WO_4H_2O$) or yellow tungstic acid ($H_2WO_4$). Breaks at these Na : W ratios would, however, be expected from metatungstic acid on the basis of the formula $H_6[H_2W_{12}O_{40}]$. This acid is produced by acidification of a soluble metatungstate. Alkali metatungstates, however, are normally prepared by slow acidification of normal or paratungstate solution kept at the boiling point during the whole period of acidification, to facilitate attainment of true equilibrium. In the method described above the sodium tungstate was passed slowly through the column at room temperature, the whole operation taking not more than 30 min. The material was examined for the presence of metatungstic acid by passing a concentrated solution of sodium tungstate (3 g/30 ml) through a column and extracting the material produced with equal quantities of ether alone, and a mixture of ether and 12 N sulphuric acid. In neither case was any trace of the heavy oily ether-metatungstic acid complex obtained. In the latter case an emulsion containing quantities of a pale yellow solid was obtained. A small quantity of the concentrated tungstic acid from the column which was allowed to stand gelled within 3 hr, and on standing

[3] E. Richardson, Ph.D. Thesis, London (1956).

overnight became a white paste. The tungstic acid produced in more dilute solution is unstable and precipitates material from solution within a fairly short while; metatungstic acid, however, is said to be stable in dilute solution.[4]

REMY[1] states that tungstates of nominal composition $R_2O : WO_3 = 1 : 4$ may be of two types, viz. salts of metatungstic acid $M'_6[H_2W_{12}O_{40}]$ and salts of hexatungstic acid $M'_3[H_3W_6O_{21}]$. The ion $[H_3W_6O_{21}]^{3-}$ is thought both by JANDER[5] and by SOUCHAY[6] to exist in acid solutions of tungstates and to be formed from $[HW_6O_{21}]^{5-}$ paratungstate *A* (the ion thought to exist in paratungstate solutions formed by rapid reaction of $WO_4^{2-}$ ions and hydrogen ions). The transformation of $[HW_6O_{21}]^{5-}$ into $[H_3W_6O_{21}]^{3-}$ is believed by JANDER to involve a third ion

$$2H^+ + [HW_6O_{21}]^{5-} \rightleftarrows H_2[HW_6O_{21}]^{3-} \rightleftarrows [H_3W_6O_{21}]^{3-}$$

The transformation $6[WO_4]^{2-} + 7H^+ \rightleftarrows [HW_6O_{21}]^{5-} + 3H_2O$ is thought both by JANDER[5] and by SOUCHAY[6] to be rapid at pH 6·8. Recent isotope exchange studies by SPITZIN,[7] however, have shown that this reaction is not instantaneous at pH 6·8 and room temperature, but is accelerated by decrease in pH and increase in temperature. Under the conditions employed in the ion-exchange experiments described (i.e. 18–20°C, time of exchange 30 min) it would seem extremely doubtful that a further reaction occurs, i.e. the conversion of paratungstate ions to metatungstate which is known to be slow. It appears much more probable that formation of paratungstate ion and subsequent conversion temporarily to the metastable free acid $H_3[H_3W_6O_{21}]$ is facilitated by the strongly acid nature of the resin. Sodium tungstate in dilute solution (3 g/100 ml) does not precipitate white tungstic acid immediately after acidification. In some experiments carried out in this laboratory several hours elapsed before precipitation. It seems possible, therefore, that the unstable hexatungstic acid $H_3[H_3W_6O_{21}]$ is the precursor of white tungstic acid.

The course of the titration shown in Fig. 1 thus has the following essential stages:

$$H_3[H_3W_6O_{21}] + 3NaOH \rightleftarrows Na_3[H_3W_6O_{21}] + 3H_2O \qquad (1)$$

$$Na_3[H_3W_6O_{21}] \overset{Na^+}{\rightleftarrows} Na_5[HW_6O_{21}] \overset{Na^+}{\rightleftarrows} Na_2WO_4 \qquad (2)$$

At the concentrations and ionic strengths used in the experiments described, in some thirty titrations breaks in the conductivity curves were noted only for the initial neutralization (1) and the final conversion to $Na_2WO_4$ (2). MAIR[8] has noted during the titration of $Na_2WO_4$ with strong acids even at the boiling point, where true equilibrium is reached and metatungstate ions are formed, that breaks corresponding to paratungstate formation were only observed at high ionic strengths (1 M NaCl).

2. *Transformation of soluble tungstic to white tungstic acid*

Complex formation between polyhydroxy compounds and inorganic acids is known to increase the solubility of many acids in aqueous solution. In a further

[4] F. EPHRAIM, *Inorganic Chemistry* (6th Ed.), p. 522. Oliver and Boyd (1954).
[5] G. JANDER and U. KRUERKE, *Z. Anorg. Chem.* **265**, 244 (1951).
[6] P. SOUCHAY, *Ann. Chim.* **18**, 73 (1943); **18**, 169 (1943).
[7] V. I. SPITZIN, International Conference on Radioisotopes in Scientific Research, 1958. UNESCO/NS/RIC/37.
[8] J. A. MAIR, *J. Chem. Soc.* 2364 (1950).

experiment the effect of typical neutral polyhydroxy compounds, viz. mannitol, erythritol, inositol, and glucose, on the transformation of the above acid into sparingly soluble white tungstic acid was followed conductometrically. The decrease in conductivity with time of a solution of tungstic acid prepared by ion exchange is shown in Fig. 2, from which it can be seen that mannitol influences the conductivity more

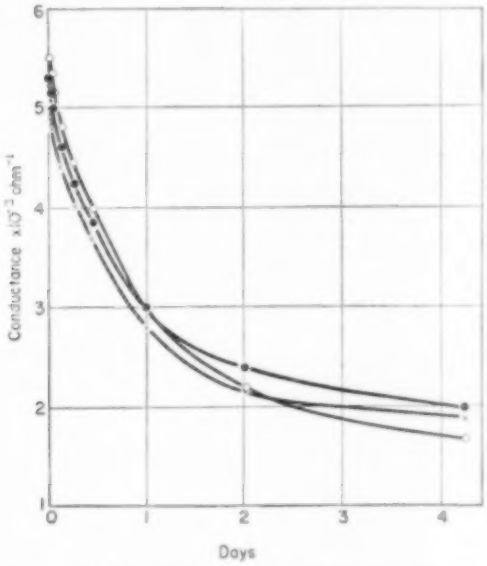



FIG. 2.—Influence of polyhydroxy compounds on the conductivity of tungstic acid.
Conductance $\times 10^{-3}\ \Omega^{-1}$ against days.
○ = Mannitol.
● = No organic compound.
× = Glucose, inositol, erythritol, pentaerythritol.
Both solutions 0·065 M (with respect to $WO_3$).

than any of the other polyhydroxy compounds. Initially, addition of mannitol causes a slight increase in the conductivity of the solution and even after several hours the conductivity of the mannitol solution is greater than the blank. The effect is quite reproducible and is not caused by impurities in the mannitol, the conductivity of which is negligible in comparison with that of the tungstic acid. After the first day, however, the conductivity of the mannitol solution was lower than that of the other solutions. Within experimental error the conductivity of the solutions containing pentaerythritol, inositol, glucose and erythritol were all equal, and at any particular time were lower than that of aqueous tungstic acid. No appreciable difference was noted in the time required for the first appearance of a definite turbidity in any of the solutions. All the solutions reached equilibrium (as measured by constant conductance) after five to six weeks, with a final conductance of $1{\cdot}3 \times 10^{-3}\ \Omega^{-1}$, except for mannitol ($1{\cdot}1 \times 10^{-3}\ \Omega^{-1}$).

Vol.
12
59/60

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 84 to 89. Pergamon Press Ltd. Printed in Great Britain.

# THE PREPARATION, PRESERVATION AND SEPARATION OF URANIUM TETRACHLORIDE AND URANYL CHLORIDE IN WATER, ETHANOL AND WATER–ETHANOL SOLVENTS

J. D. HEFLEY, D. M. MATHEWS and E. S. AMIS
Chemistry Department, University of Arkansas, Fayetteville, Arkansas

(*Received* 30 *July* 1958; *in revised form* 25 *February* 1959)

**Abstract**—The sublimation of $UCl_4$ under argon and nitrogen is discussed. The former gave 99·42 per cent $UCl_4$ which yielded a stable solution free from colloid formation. The sublimation under nitrogen yielded a brownish-red material which had the combustibility and solubilities associated with the nitride but which was shown to be $UO_2$ by X-ray spectrum analysis. Both stabilities of the $UCl_4$ solutions and their analyses for uranium by the use of cupferron are discussed for both water and ethanol solvents.

The preparation of pure $UO_2Cl_2 \cdot H_2O$ is described, and the stability data for $UO_2Cl_2$ solutions in water, ethanol and water–ethanol solvents are presented.

The cupferron method of separation of U(IV) and U(VI) was found to be as effective.

Vol.
12
1959/6

LITTLE is known of the properties of solutions of uranyl chloride and uranium tetrachloride in pure non-aqueous solvents and in mixed solvents composed of water and non-aqueous components. There is only limited reference in the literature to the stability of aqueous solutions of these solutes.

KRAUS and NELSON[1] determined the acid equilibrium constants for the practically instantaneous hydrolysis of $U^{4-}$ and $Pu^{4-}$ ions to $UOH^{3-}$ and $PuOH^{3-}$ ions. They likewise observed additional slow hydrolytic reactions and found that the aggregates of the hydrolysis products reached colloidal size. RONA[2] mentions dissolving uranium tetrachloride in oxygen-free water solutions of hydrochloric acid. She also ran the electron exchange reaction between U(IV) and U(VI) ions in aqueous solution under nitrogen as a precaution against oxidation of the U(IV) to U(VI).

RONA[2] used hydrofluoric acid as a reagent for separating U(IV) and U(VI). In this investigation it was found that for complete separation of U(IV) from U(VI) the hydrofluoric acid had to be relatively high in concentration. Since the separations were to be carried out using glass equipment, concentrated hydroflouric acid was unsatisfactory as a reagent.

HILLEBRAND *et al.*[3] describe the separation in water solution of U(IV) and U(VI) using cupferron. It was not known that this separation could be effected using mixed or nonaqueous solvents.

(1) K. A. KRAUS and F. NELSON, *J. Amer. Chem. Soc.* **72**, 3901 (1950).
(2) E. RONA. *J. Amer. Chem. Soc.* **72**, 4339 (1950).
(3) W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT and J. I. HOFFMAN, *Applied Inorganic Analysis* (2nd Ed.), p. 116. John Wiley, New York (1953).

Solutions of uranium tetrachloride and of uranyl chloride were needed for conductance and electron exchange rate investigations. Because of the difficulties encountered in preparing, preserving and analysing these solutions the following studies were made.

## EXPERIMENTAL AND RESULTS

*Preparation of uranium tetrachloride solution*

The starting materials used in this investigation were

(a) Commercial grade $UCl_4$ obtained from MacKay Chemical Company. This product was spectroscopically pure.

(b) Vacuum sublimed $UCl_4$ prepared from commercial grade $UCl_4$.

A distilled water solution about 1·5 M in substance (a) and about 0·3 N in hydrochloric acid was prepared, the remaining solid shown by preliminary analysis to be $U_3O_8$, centrifuged out, the supernatent solution decanted and diluted to about 0·02 N in hydrochloric acid. After 48 hr a black colloid formed in the solution. This colloid could not be broken by freezing, heating, changing the pH, or subjecting it to an electric current. An 0·8 M solution of substance (a) in distilled water, centrifuged and decanted as described above, was stable for 72 hr at 0°C when kept in a sealed tube. A sample withdrawn from this solution after 48 hr became colloidal after 24 hr at room temperature.

After various attempts to make a stable uranyl tetrachloride solution by varying the acidity, the uranium concentration, the method of mixing the components and the temperature of the components being mixed, it was concluded that the oxygen dissolved in the solvent water and the impurities present in material (a) were responsible for the colloid formation.

A stable solution of material (a), however, was made by boiling distilled water and cooling it under nitrogen. Using a nitrogen atmosphere, a solution of $UCl_4$ was prepared and treated as follows. A solution of material (a) about 0·15 M was prepared using this solvent by dissolving 15 g of (a) in 30 ml, decanting off about 25 ml of the supernatent liquid and splitting the 25 ml into equal portions and diluting each to 100 ml. Each flask was stoppered with a greased, ground-glass stopper. One flask was kept at 0°C and the other at room temperature. Neither solution showed colloid formation after ten days.

*Observation on sublimation of* $UCl_4$ *in nitrogen*

Although material (a) contained no foreign elements, it was evident that compounds of uranium other than $UCl_4$ were present. Therefore, the compound was purified further by sublimation.[4] The first attempts to sublime material (a) were conducted in a nitrogen atmosphere at about 3 mm pressure and the temperature of a Meker burner about 700–900°C. Resublimations under the same conditions of temperature and pressure resulted in less and less uranium tetrachloride and more and more of a brownish-red, easily sublimed compound. The brownish-red material burned in air, dissolved in concentrated nitric acid and was insoluble in water, hydrochloric acid, and sodium hydroxide. These properties of the compound (see reference 4, pp. 240–1) together with the fact that it was prepared by subliming $UCl_4$ in an atmosphere of 99·7 per cent nitrogen, led us to believe that the compound was a nitride of uranium, even though no ammonia was detected when the compound was placed in molten alkali.

The X-ray spectrum, however, revealed only $UO_2$ diffraction lines. This data indicates that the brownish-red material is the dioxide.

*Sublimation of* $UCl_4$ *in argon*

In these experiments, the pressure and the temperature were the same as when nitrogen was used. The middle portion was collected. This material (b) had a chloride to uranium ratio of 3·94 and had a purity of 99·42 per cent $UCl_4$ as calculated from the amount of chloride present. The solid uranium tetrachloride (1·5448 g) taken from analysis dissolved completely in 25 ml of distilled water without any precautions being taken to remove oxygen or to prevent air from coming in contact with the

[4] J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium* (1st Ed.), Vol. 5, p. 475. McGraw-Hill, New York (1951).

$UCl_4$ or the solution. Observations of this solution over a 72 hr period showed no colloid formation.

The stable uranium tetrachloride solution prepared from the sublimed material (b) was analysed for uranium by using the cupferron procedure.[3,5] In this method, 5 ml of six normal hydrochloric acid are added to 5 ml of the uranium tetrachloride solution, then 5 ml of a 1·0 molar solution of cupferron are slowly added to precipitate the tetravalent uranium. A few drops of cupferron are added to test for completeness of precipitation. (See Table 1 for data on a typical analysis.) The precipitate is then collected on a filter paper and burned to $U_3O_8$ at 1200°C.[6] The acidity of the solution used in this analysis is greater than that of the usual cupferron procedure; this is necessary to prevent the precipitation of hexavalent uranium, if any is present. HOLLADAY and CUNNINGHAM[7] also found that an increased acidity is necessary in the analysis of tetravalent uranium. Some references[8,9] have indicated that a reducing agent such as hydroxylamine or sodium dithionite should be present in the cupferron procedure to insure no oxidation of uranium (IV) and its subsequent failure to precipitate with cupferron, but tests for completeness of precipitation when the precipitation of uranium (IV) was performed without these reducing agents have not indicated the need for them.

The analysis for $U_3O_8$ did not vary over a two-week period if the solutions were kept under nitrogen in a flask sealed with a greased ground-glass stopper. There was slow oxidation of the uranium (IV) to uranium (VI) if these precautions were not observed.

The solution prepared from the sublimed uranium tetrachloride was analysed for uranium by oxidizing to uranyl with nitric acid and evaporating to dryness in a porcelain crucible. The residue was then burned to $U_3O_8$.[6,10,11] The results of these analyses are also shown in Table 1. It is

TABLE 1.—ANALYSIS OF $UCl_4$ IN WATER

| Cupferron method | Oxidation by nitric acid |
|---|---|
| The amounts of materials taken for each analysis. | The amounts of materials taken for each analysis. |
| 5 ml of $UCl_4$ containing uranium equivalent to 0·08210 g of $U_3O_8$.<br>5 ml of 6 N HCl<br>5 ml of 1·0 M cupferron | 5 ml of $UCl_4$ containing uranium equivalent to 0·08210 g of $U_3O_8$.<br>A few drops of conc. $HNO_3$ |
| Wt. of $U_3O_8$ found | Wt. of $U_3O_8$ found |
| I 0·08208<br>II 0·08212<br>III 0·08210 | I 0·0817<br>II 0·0818<br>III 0·0817 |
| Ave. 0·08210 ± 0·00001<br>% deviation from theoretical = 0·00 | Ave. 0·0817 ± 0·00003<br>% deviation from theoretical = 0·49 |

observable that while these results were not weighed to the same number of decimals, they gave high precision. The average value by this method was slightly less than 0·5 per cent lower than that

[5] C. J. RODDEN, *Analyt. Chem.* **25**, 1598 (1953).
[6] R. J. BROUNS and W. W. MILLS, HW-39767, Hanford Atomic Productions Operation, Richland, Wash. (1955).
[7] J. A. HOLLADAY and T. R. CUNNINGHAM, *Trans. Amer. Electrochem. Soc.* **43**, 329 (1923).
[8] N. H. FURNHAM, W.B. MASON and J. S. PEKOLA, *Use of Cupferron in the Estimation of Uranium*, Princeton University, ACMP Collected Paper, 49, April 1946.
[9] E. M. KINDERMAN, B. M. TOLBERT, E. ZEBROSKI and E. H. HOFFMAN, R-L 4.6.293, Sept. 30, 1944.
[10] I. M. KOLTHOFF and E. B. SANDELL, *Textbook of Quantitative Inorganic Analysis*, (3rd Ed.) pp. 303–308, MacMillan, New York (1952).
[11] N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis* (5th Ed.), Vol. 1. Van Nostrand, New York (1939).

Vol. 12 1959/6

obtained by the cupferron method. The chloride was determined by the usual gravimetric method.[12] The purity and the chloride to uranium ratio mentioned above were calculated from the results of these analyses.

A solution of spectroscopically pure uranium tetrachloride (material a) in 100 per cent ethanol was prepared in the following manner. Twenty-five grammes of uranium tetrachloride obtained from the MacKay Chemical Company were mixed with 30 ml of 100 per cent ethanol and centrifuged to remove the black solid. The solution was then decanted into a flask, diluted to 500 ml with 100 per cent ethanol, flushed with nitrogen, and stoppered with a greased ground-glass stopper. Analyses, extending over a period of two weeks, showed no deterioration of the solution when kept under nitrogen.

In a similar manner, a stable solution was prepared in anhydrous ethanol using the sublimed product.

The solutions of uranium tetrachloride in 100 per cent ethanol were analysed by the following procedure. Two millilitres of the uranium tetrachloride were added to 8 ml of distilled water, 10 ml of 6 N hydrochloric acid were added to the uranium solution and the tetravalent uranium was then precipitated by slowly adding 10 ml of a 0·12 molar solution of cupferron. Precipitation was found to be complete. (See Table 2 for typical data.) Since uranium tetrachloride of 99·42 per cent purity

TABLE 2.—CUPFERRON ANALYSIS OF $UCl_4$ IN PURE ETHANOL

| | | |
|---|---|---|
| Conc. cupferron = 0·12 M | | |
| Wt. $U_3O_8$ | I | 0·04808 |
| | II | 0·04817 |
| | III | 0·04818 |
| Ave. | | 0·04814 ± 0·0004 |
| Amt. of $U_3O_8$ theoretical = 0·04824 | | |
| Per cent error = $\frac{0{\cdot}04824 - 0{\cdot}04814}{0{\cdot}04824} \times 100 = 0{\cdot}25$ | | |

was used in making the solutions, the chloride uranium ratio was not determined.

The precision of the uranium tetrachloride analyses in 100 per cent ethanol was 0·1 per cent.

*Preparation of uranyl chloride solutions*

The easiest way that could be found to prepare a uranyl chloride solution was to use uranyl nitrate hexahydrate, obtained from the Mallinkrodt Chemical Company, as the starting material. This compound was dissolved in concentrated hydrochloric acid and evaporated by distillation until the medium was very viscous. At this point, concentrated hydrochloric acid was added in small portions until no brown oxides of nitrogen could be seen. The evaporation was continued in this manner until the brucine test[13] indicated that no nitrate was present in the solution. When no nitrate could be detected, addition of HCl was stopped and water was added. The evaporation was continued until analysis showed the chloride to uranium ratio to be less than two. Solutions of the desired concentrations were made from this material with the addition of the proper amount of standard HCl solution.

Aqueous solutions of uranyl chloride were found to be stable for an indefinite length of time. Table 3 shows the stability of uranyl chloride solutions in the indicated water–ethanol solvents. The decomposition times noted in Table 3 are definitely not clear-cut quantities. The decomposition times indicated for the solutions that contained water[3,6–8] is the time that a white solid could definitely be seen on the wall of the flask. The decomposition in the absolute ethanol solution manifested itself as a very gradual colour change from the original yellow to a dark red. Soon after the formation of the dark red colour, a black, flocculant precipitate formed. The time that this precipitate formed is the decomposition time recorded.

[12] W. C. PIERCE and E. L. HAENICH, *Quantitative Analysis* (3rd Ed.), p. 380. John Wiley, New York (1944).
[13] F. FEIGL, *Spot Tests* (4th Ed.), Vol. 1, p. 300. Elsevier, New York (1954).

The solutions were tested for the effect of light by storing them in dark bottles. No effect of light was observed by our criterion of stability.

*Preparation of uranyl chloride monohydrate*

There are recorded many high temperature methods of preparation of anhydrous uranyl chloride.[4,14] These methods are, at best, difficult and inconvenient. Moreover, purification of the compound formed at high temperatures is, if at all possible, very tedious. By use of the method described below, uranyl chloride monohydrate can be prepared by use of common equipment and chemicals without resorting to high temperature methods.

Table 3.—Stability of $UO_2Cl_2 \cdot H_2O$ solutions

| Soln. No. | Conc. $UO_2Cl_2$ (M) | Solvent (vol. % $C_2H_5OH$) | Time of decomposition (days) |
|---|---|---|---|
| 1 | 0·022 | 100 | 13 |
| 2 | 0·028 | 100 | 11 |
| 3 | 0·051 | 100 | 11 |
| 4 | 0·067 | 100 | 11 |
| 5 | 0·096 | 100 | 11 |
| 6 | 0·050 | 20 | No decomposition after 16 |
| 7 | 0·050 | 40 | 10 |
| 8 | 0·050 | 60 | 7 |
| 9 | 0·050 | 80 | 9 |

This method of preparation is exactly as that described above up to the point where an absence of nitrate is indicated by the brucine test. At this point, the flask is transferred to an oil bath maintained at 180°C and dry HCl gas is kept flowing over the product. The material is stirred rapidly with the inlet tube of the HCl gas to prevent the product from hardening into a rock-like mass. When the material is solid and appears dry, heating is stopped and the crushed compound covered with freshly distilled thionyl chloride. Refluxing speeds up the further dehydration considerably but it is not essential. Upon dehydration, the lumps of hydrated uranyl chloride form a light yellow powder having an appearance very similar to powdered sulphur. The excess thionyl chloride is decanted and the flask connected to a water aspirator through a drying tube. The flask is warmed gently in a water bath until no liquid can be seen in the flask, at which time it is transferred to a vacuum drying oven maintained at 80°C and allowed to dry there for 1 hr. Uranyl chloride monohydrate ($UO_2Cl_2 \cdot H_2O$) prepared in this manner has been analysed to have a purity of 99·99 per cent and a chloride to uranium ratio of 2·000. This compound absorbs moisture rapidly and must be handled in a dry atmosphere.

From the determination of uranium as $U_3O_8$, the percentage of $UO_2Cl_2$ in the compound was found to be 94·81 and 94·87. From the analyses for chloride, the percentage of $UO_2Cl_2$ in the compound was found to be 94·93 and 94·82. The average of all these is 94·86 ± 0·04. The theoretical percentage of $UO_2Cl_2$ in $UO_2Cl_2 \cdot H_2O$ is 94·99. The percentage deviation of the analysed from the theoretical per cent is 0·19 per cent. This deviation is less than 0·2 parts per thousand.

Since Mallinkrodt reagent grade uranyl nitrate was used in the preparation of the uranyl chloride, since no traces of nitrogen were left in the product, and since analyses for both $U_3O_8$ and chloride agreed so precisely, the criterion for per cent purity and composition of the product was based on the agreement between the analysed and theoretical per cent of $UO_2Cl_2 \cdot H_2O$. No actual water determination was made since the one water is bound so tightly by uranyl chloride that any water analysis would be very doubtful as to the completeness of the determination.

[14] N. V. Sidgwick, *Chemical Elements and Their Compounds* Vol. 2, p. 1076. Oxford University Press, London (1956).

Vol. 12 1959/6

Although the $UO_2Cl_2 \cdot H_2O$ contains a mole of water, this compound can be satisfactorily used in non-aqueous solvents whenever the small weight per cent of water is not deleterious. For example, a one molar solution in anhydrous ethyl alcohol would only introduce 2·2 per cent water.

*Separation of* U(IV) *from* U(VI)

Cupferron as a method of separation was found to be satisfactory for the separation of U(IV) from U(VI) in both water and alcohol solutions. The separations were performed in the following manner. One millilitre of six normal hydrochloric acid was added to 1 ml of either an aqueous, an alcoholic, or an ethanol–water solution of U(IV) and U(VI). The U(IV) and U(VI) were each 0·025 molar.

It was found that the moles of cupferron must be somewhat in excess of four times the number of moles of U(IV) present. However, if the number of moles of cupferron exceeded eight times the number of moles of U(IV), the U(VI) was also partially precipitated. One millilitre of 0·12 molar cupferron was added to precipitate the U(IV). The solution was then centrifuged and the supernatent solution of hexavalent uranium was decanted from the tetravalent precipitate and the completeness of separation tested by further addition of cupferron solution to the U(VI) solution.

Since it has been proven that the concentration of tracer in an exchange system reaches a point of equilibrium that is dependent only on the total concentration of the materials involved,[15] this fact was used as a final test of the separation procedure described above. In this process, 100 $\lambda$ of 0·005 M $^{233}U$ was added as the nitrate to 10 ml of a solution containing 0·1 M $UCl_4$ and 0·1 M $UO_2Cl_2$ in absolute ethanol and allowed to stand for one day so that the exchange would be complete. The solutions to be tested were prepared by taking 2 ml of the stock solution and diluting to 10 ml with the desired solvent. The U(IV) was precipitated and 50 $\lambda$ portions of the supernatant U(VI) solutions were counted. As is shown in Table 4, the same separation was effected in all solvent compositions tested within the limits of counting accuracy.

TABLE 4.—SEPARATION OF U(IV) AND U(VI)

| Solvent (vol. % ethanol) | Counts/min |
|---|---|
| 13·3 | 2057 ± 42 |
| 20 | 2031 ± 41 |
| 40 | 2092 ± 44 |
| 50 | 2148 ± 46 |

The tetravalent cupferrate can be put back into solution by washing the precipitate with water and then dissolving it in acetone or chloroform.[16]

## CONCLUSION

By careful manipulations, pure $UCl_4$ and $UO_2Cl_2 \cdot H_2O$ can be easily obtained, the former compound by sublimation of commercial $UCl_4$ and the latter by the method of preparation given in this manuscript. The stability of solutions of $UO_2Cl_2$ is dependent on the solvent composition used. A high purity $UCl_4$ in an oxygen free solvent is the most stable in any solvent composition studied.

The cupferron method of separation of U(IV) and U(VI) was found to be effective in ethanol, and in water–ethanol solvents as in water alone.

*Acknowledgement*—We wish to express our thanks to the Atomic Energy Commission for the financial support of this work on Contract AT-(40-1)-2069 and to Drs. G. P. SMITH and H. L. YAKEL for the X-ray spectrum work reported in this manuscript.

[15] R. B. DUFFIELD and M. CALVIN, *J. Amer. Chem. Soc.* **68**, 557 (1946).
[16] C. J. RODDEN, *Analyt. Chem.* **21**, 327 (1949).

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 90 to 94. Pergamon Press Ltd. Printed in Great Britain.

# AMMONOLYSIS OF PERCHLORYL FLUORIDE*

H. C. MANDELL, JR. and G. BARTH-WEHRENALP

Pennsalt Chemicals Corporation, Research and Development Department, Wyndmoor, Pa.

(*Received* 23 *February* 1959)

**Abstract**—Perchloryl fluoride ($ClO_3F$) reacts with aqueous or liquid anhydrous $NH_3$ to form a mixture of $NH_4F$ and $NH_4NHClO_3$. Ammonolysis of $ClO_3F$ in liquid $NH_3$ is greatly accelerated by traces of $NaNH_2$ (base catalysis).

From an aqueous solution of $NH_4F + NH_4NHClO_3$, concentrated aqueous or alcoholic solutions of caesium or potassium hydroxides precipitate salts of the types $K_2NClO_3$ and $KNHClO_3$. The former are isomorphous with the corresponding metal sulphates. The latter are nearly isomorphous with the corresponding perchlorates. These salts are highly explosive, and when dry are very sensitive to flame, shock and friction. Potentiometric titration of $K_2NClO_3$ with strong acid gives a curve corresponding to the ionization of the amide $ClO_3NH_2$:

$$H_2NClO_3 \rightleftharpoons H^+ + HNClO_3^- \quad (pH = 3{\cdot}7)$$

$$HNClO_3^- \rightleftharpoons H^+ + NClO_3^{2-} \quad (pH = 8{\cdot}6)$$

The identity of the ions $NHClO_3^-$ and $NClO_3^{2-}$ was further established by ion exchange analysis.

ENGELBRECHT[1] reported that liquid perchloryl fluoride reacts slowly with anhydrous $NH_3$ at $-78°C$ to form $NH_4F + NH_4NHClO_3$. Several hours were required for a few grammes of product to be formed. The compound $NH_4NHClO_3$, regarded as the ammonium salt of the acidic amide $H_2NClO_3$, was not isolated.

In further study of the reaction of $ClO_3F$ with $NH_3$, it was found that liquid $NH_3$ at $-78°C$ saturated with sodamide, $NaNH_2$, reacted within a few minutes with liquid $ClO_3F$, according to the same reaction proposed by Engelbrecht.

$$ClO_3F + 3NH_3 \longrightarrow NH_4F + NH_4NHClO_3 \qquad (1)$$

There was no reaction between $ClO_3F$ and $NaNH_2$ itself. These results are analogous to the observed reactions of $ClO_3F$ with water and NaOH.

$$ClO_3F + H_2O \longrightarrow \text{(extremely slow) } HClO_4 + HF \qquad (2)$$

$$ClO_3F + NaOH \longrightarrow NR \qquad (3)$$

$$ClO_3F + H_2O \xrightarrow{(NaOH)} \text{(relatively rapid) } NaClO_4 + NaF \qquad (4)$$

The reaction of $ClO_3F$ with $NH_3$ is thus regarded as a base catalysed solvolysis. Reaction (1) also was found to occur slowly between $ClO_3F$ and concentrated aqueous $NH_4OH$.

ENGELBRECHT[1] made unsuccessful attempts to separate pure $NH_4NHClO_3$ from the simultaneously formed $NH_4F$ by fractional sublimation and crystallization. The following method for isolating pure soluble perchloramide salts has now been developed.

* Presented before the Division of Industrial and Engineering Chemistry, American Chemical Society 134th Meeting, September 11, 1958.

[1] A. ENGELBRECHT and H. ATZWANGER, *J. Inorg. Nucl. Chem.* **2**, 348 (1956).



Vol. 12 1959/6

It was found that the potassium and caesium (and probably the rubidium) salts of perchloramide are sufficiently insoluble to be precipitated from the aqueous $NH_4F + NH_4NHClO_3$ solution by addition of a very high concentration of those cations. When a dilute solution of $NH_4F + NH_4NHClO_3$ was saturated with solid KOH or was mixed with an equal volume of 90 per cent ethanol saturated with KOH (a ten- to fifteen-fold excess of KOH), the fine, white crystalline precipitate which formed proved to be $K_2NClO_3$. When a much smaller excess (threefold) of base was used, a white crystalline precipitate of $KNHClO_3$ formed. Similar products precipitated when $K_2CO_3$ was used in place of KOH. When CsOH was used, the analogous caesium salts formed.

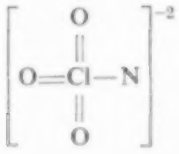
These new compounds were evidently the alkali metal salts of the acidic amide of perchloric acid. They were formed by displacing the more weakly basic ammonium ion and by neutralizing the other weakly acidic proton in the amide.

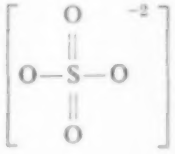
$$NH_4NHClO_3 + 2KOH \longrightarrow K_2NClO_3 + NH_4OH + H_2O$$

When smaller excess of strong base was employed, the replacement of the ammonium ion took place without neutralization of the other proton.

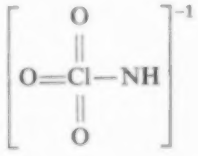
These non-hygroscopic crystalline white materials, $KNHClO_3$, $K_2NClO_3$, $CsNHClO_3$ and $Cs_2NClO_3$, proved to be extremely soluble in water but very slightly soluble in 75 per cent or stronger ethanol. They were found stable indefinitely at room temperature and were heated to over 300°C in capillary tubes without melting or decomposing. All were, however, powerful explosives, being very sensitive to shock, friction or open flame, especially when dry. Great care always had to be taken in removing the dried solids from the filtration vessel. $KNHClO_3$, $K_2NClO_3$ and $Cs_2NClO_3$ were seen to crystallize in very small prisms while $CsNHClO_3$ formed large octahedral plates. The X-ray diffraction patterns of the dimetal salts were identical with those of the corresponding sulphates while the patterns for the mono-salts were similar to the corresponding perchlorate patterns.

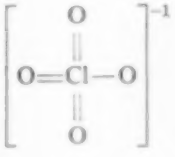
The basis for the similarity may be seen in the structures of the ions involved.



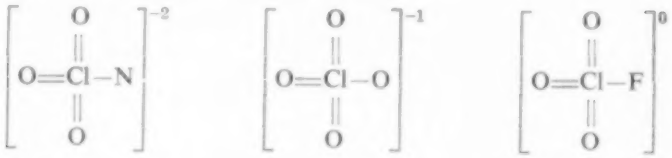

The covalent atomic radii for chlorine and sulphur and for nitrogen and oxygen are virtually identical.




The structure of $NHClO_3^-$ would be anticipated to be much like that of $ClO_4^-$.

Interesting to note is the series of stable ions:



in which nitrogen, oxygen and fluorine of similar electro-negativities and nearly identical sizes occupy tetrahedral places with oxygen atoms about a central chlorine atom.

Titration of a dilute solution of an alkali metal perchloramide, as illustrated in Fig. 1 gave inflexions in a potentiometric curve corresponding to the reactions

$$H^+ + NClO_3^{2-} \rightleftharpoons HNClO_3^- \quad (pH\ 8{\cdot}6)$$

$$H^+ + HNClO_3^- \rightleftharpoons H_2NClO_3 \quad (pH\ 3{\cdot}7)$$

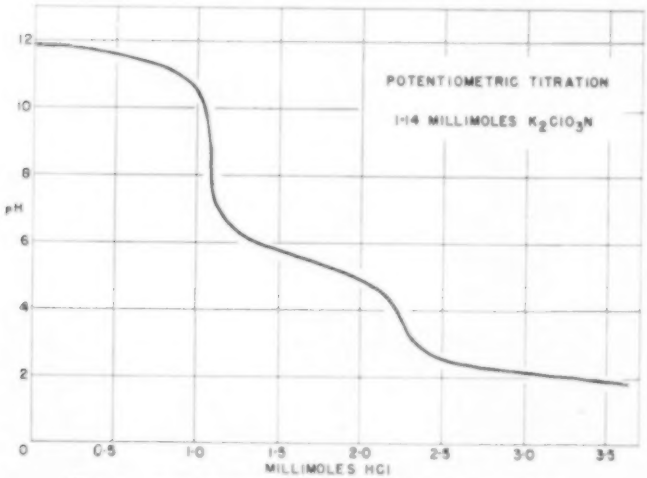



FIG. 1.—Potentiometric titration of $K_2NClO_3$ with HCl.

From these values can be calculated the dissociation constants for the amide $H_2NClO_3$

$$K_1 = 3{\cdot}0 \times 10^{-6} \quad : \quad K_2 = 1{\cdot}1 \times 10^{-12}$$

The amide is thus an acid of roughly the same strength as carbonic acid for which $K_1 = 3{\cdot}5 \times 10^{-7}$ and $K_2 = 4{\cdot}4 \times 10^{-11}$. This suggests that dimetal salts of perchloramide can be prepared from solution for only the most basic cations, alkali and alkaline earth metals, and explains the existence of only the monoammonium derivative.

By simple metathesis, these soluble akali metal perchloramides, free of fluoride, can be converted to many other perchloramides. For example, a solution of $K_2NClO_3$ was titrated to pH 8·5 with $HClO_4$. Insoluble $KClO_4$ was recovered and evaporation of the filtrate gave crystalline $KNHClO_3$.

In attempt to prepare pure $NH_4NHClO_3$ by a similar procedure, a solution of $K_2NClO_3$ was acidified to pH 3·5 with dilute $HClO_4$. Reduction of the volume by vacuum evaporation and subsequent addition of alcohol permitted precipitation of

Vol. 12 1959/6

all of the potassium as $KClO_4$. When excess $NH_4OH$ was added and the evaporation continued, there was decomposition with the evolution of chlorine as the solution became concentrated. The solid finally obtained was about 20 per cent $NH_4NHClO_3$.

Likewise, an effort to isolate $H_2NClO_3$ by precipitating all the potassium from $K_2NClO_3$ and evaporating the resulting solution, gave a solution of $H_2NClO_3$ that was stable only until it was concentrated.

It has been previously reported[1] that solutions of $NH_4NHClO_3 + NH_4F$ decomposed when made acid. One of the products was said to be chlorate ion, although the hydroxylamine which should have been simultaneously formed could not be detected. The potentiometric titrations of $K_2NClO_3$ gave no evidence of decomposition of $H_2NClO_3$ at pH 2 or above. Analysis was made of some slightly acidic solutions of $NH_4F + NH_4NHClO_4$, using the customary iodimetric determination of chlorate. (Reduction with KBr, addition of KI and titration of the $I_2$ liberated.) The "chlorate" determined thus by reduction was found to be one third more than the total chlorine content of the sample determined by reduction with $Ti_2(SO_4)_3$ and titration of the resulting $Cl^-$. This suggests an eight rather than six electron change upon reduction of acidified perchloramide solutions. The conclusion is that heptavalent and not pentavalent chlorate chlorine was present. Since perchlorate ion is not reduced by KBr in dilute acid, the heptavalent chlorine must have been in another form, probably $H_2NClO_3$. Only when the strength of a mineral acid was increased to a few molar was there obvious decomposition of perchloramide solutions into chlorine and oxygen.

To confirm the nature of the ion $NClO_3^{2-}$, and to demonstrate that the stable perchloramide is reduced as readily as chlorate, some ion exchange studies were carried out. Dilute solutions containing 8·56 mmole each of $K_2NClO_3$ were passed through cation exchange resin IR 120 and through anion exchange resin IR 400. The anionic resin was eluted with 2N NaOH, then all three effluents were analysed.

The analytical results are given in Table 1.

TABLE 1.—ION EXCHANGE OF $K_2NClO_3$ SOLUTION

| | pH | Chloride (mmole) | "Chlorate" by redox method (mmole) | 0·75 × "chlorate" (mmole) | Total chlorine by $Ti_2(SO_4)_3$ | Total nitrogen (mmole) |
|---|---|---|---|---|---|---|
| Original | 12·0 | 0·0 | 11·2 | 8·4 | 8·4 | 8·75 |
| Cation effluent | 3·7 | 0·0 | 11·6 | 8·7 | 8·4 | 8·60 |
| Anion effluent | 12·0 | 0·0 | 0·4 | 0·3 | 0·0 | 0·7 |
| Anion eluate | — | 0·0 | 10·85 | 8·14 | 8·15 | 8·12 |

These results clearly show that the chlorine and nitrogen are in an anion, that the anion is stable at pH 3·7 and that the heptavalent chlorine present is reduced as easily as chlorate.

## EXPERIMENTAL

*Ammonolysis of* $ClO_3F$

In a glass trap was placed about 0·1 g $NaNH_2$. This was cooled with liquid nitrogen and on it were condensed 18 mmoles of $ClO_3F$ and 75 mmoles of $NH_3$. When warmed to −78°C, the solids melted into two phases which reacted in 3–4 min giving a white solid. From this solid was recovered 20 mmoles of unreacted $NH_3$.

When 10 mmoles of $ClO_2F$ were condensed on 0·1 g of $NaNH_2$, the solid showed no sign of dissolving at −78°C. The $ClO_2F$ was recovered unchanged (IR spectrum) and the solid was found to contain no fluoride or chlorine compound.

*Preparation of* $K_2NClO_2$

A slow stream of $ClO_2F$ was bubbled through concentrated aqueous reagent $NH_4OH$ for about 3 hr resulting in a 0·4–0·5 M solution of $NH_4F + NH_4NHClO_2$. A portion of this solution was saturated with solid KOH, whereupon a fine white solid precipitated. When filtered on sintered glass, washed with 95 per cent ethanol and dried at 110°C, this solid analysed 8·1% N, 44·3% K, 20·5% Cl and 0·3% F. Calculated for $K_2NClO_2$ is 8·0% N, 44·5% K and 20·2% Cl. (Total chlorine by reduction with $Ti_2(SO_4)_3$, total nitrogen by Dumas method.) A similar product was obtained by mixing equal volumes of 0·5 M $NH_4F + NH_4NHClO_2$ and a saturated solution of KOH in 90 per cent ethanol.

*Preparation of* $Cs_2NClO_2$

To 10 ml of the $NH_4F + NH_4NHClO_2$ solution were added 10 ml of 95 per cent ethanol saturated with CsOH.

Fine white crystals precipitated at once. These were filtered, washed with 85 per cent ethanol and dried at 25°C *in vacuo*. (Found Cs 72·75, Cl 9·68, N 4·18. Calc. for $Cs_2NClO_2$: Cs 73·1, Cl 9·78, N 3·85%).

*Preparation of* $CsNHClO_2$

To 10 ml of the $NH_4F + NH_4NHClO_2$ solution were added 2 ml of 90 per cent ethanol saturated with CsOH. The white crystalline precipitate was filtered and dried as described above. (Found Cs 57·6, Cl 15·6, N 5·93. Calc. for $CsNHClO_2$: Cs 57·4, Cl 15·35, N 6·05%.)

*Potentiometric titration of* $K_2NClO_2$

A Beckman model H pH meter, a blue (alkaline range) glass indicator electrode and a calomel reference electrode were used.

A 0·015 M water solution of $K_2NClO_2$ had a pH of 12. Titration of this solution with 0·1 N HCl, $H_2SO_4$ or $HClO_4$ resulted in a potentiometric curve with a sharp inflexion at pH 8·6 and a more diffuse inflexion at pH 3·7 (Fig. 1). For titrations of 1·14 mmole of $K_2NClO_2$ with HCl, the first endpoint came at 1·08 milliequivalents and the second at 2·26. These results correspond to the reactions

$$K_2NClO_2 + H^+ \rightarrow KHNClO_2 + K^+$$
$$KNHClO_2 + H^+ \rightarrow H_2NClO_2 + K^+$$

*Preparation of* $KNHClO_2$ *from* $K_2NClO_2$

A 0·5 M solution of $K_2NClO_2$ was titrated to pH 8·5 with 0·1 N $HClO_4$. By evaporating the solution to a small volume and adding about three times that volume of ethanol, there was crystallized out all of the $KClO_4$ formed. The supernatant liquid was evaporated *in vacuo* at 45°C to leave a solid that analysed 30·6% K, 27·3% Cl and 10·6% N. Calculated for $KNHClO_2$ is 28·4% K, 25·8% Cl, 10·2% N. In several preparations, the potassium and chlorine analyses were always slightly high, probably due to the formation of a little KCl by decomposition during the final evaporation.

*Acknowledgements*—The authors wish to acknowledge permission of the Pennsalt Chemicals Corporation to publish this work and to thank Mr. E. S. EITELMAN for his valuable assistance.

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 95 to 103. Pergamon Press Ltd. Printed in Great Britain.

# CATION EXCHANGE PROPERTIES OF THE AMMONIUM HETEROPOLYACID SALTS

J. VAN R. SMIT, J. J. JACOBS and W. ROBB

National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, Pretoria

(*Received* 23 *February* 1959)

**Abstract**—This paper describes the cation exchange properties of the ammonium salts of some heteropolyacids. In acidic solutions, only those metal ions that form heteropolyacid salts which are insoluble in water exchange significantly with the ammonium ions on these salts. These are the larger alkali ions: potassium, rubidium and caesium; and the monovalent ions: silver, mercury (I) and thallium (I). Mass distribution coefficients for trace amounts of these ions were obtained in 0·1 N ammonium nitrate, and they show remarkably high selectivities of the ammonium heteropolyacid salts towards these ions. Selectivity coefficients for pairs of alkali metal ions are more than ten times as high for ammonium molybdophosphate as those obtaining for the organic resin Dowex 50.

The solubility of ammonium molybdosilicate and ammonium tungstosilicate is such as to preclude their use as ion exchange materials for separating ions. In the case of ammonium molybdoarsenate, materials of different colour and physical appearance were obtained by different routes of preparation. These showed marked differences in adsorbability towards caesium. Preliminary X-ray diffraction analysis has shown these differences in ion exchange behaviour to be due to the existence of different crystallographic components in the various preparations.

Vol. 12 9/60

IT has been known for over fifty years that when an ammonium molybdophosphate precipitate is washed with potassium nitrate solution, as is customary in many procedures for the determination of phosphate by means of the molybdophosphate reaction, some of the ammonium ions in the precipitate exchange for potassium ions. BAXTER and GRIFFIN[1] who discovered this phenomenon, found the exchange to be reversible, for, after subsequent treatment of the precipitate with ammonium nitrate solution, the composition of the precipitate was the same as if the potassium nitrate treatment had been omitted.

Similar observations have since been reported by a number of workers. Washing with neutral potassium nitrate solution was found by TERLET and BRIAU[2] to produce about 50 per cent replacement of the ammonium ions. Sodium ions also exchange when the precipitate is treated with sodium sulphate solution, but to a much smaller extent. According to GISIGER,[3] the extent of exchange increases with increasing concentration of the replacing ion. THISTLETHWAITE[4] found that approximately two of the three ammonium ions are replaced by potassium when ammonium molybdophosphate is washed with a dilute acidified potassium nitrate solution.

(1) G. P. BAXTER and R. C. GRIFFIN, *Amer. Chem. J.* **34**, 204 (1905).
(2) H. TERLET and A. BRIAU, *Ann. Fals.* **28**, 546 (1935).
(3) L. GISIGER, *Z. Anal. Chem.* **115**, 15 (1938).
(4) W. P. THISTLETHWAITE, *Analyst* **72**, 531 (1947).

Base exchange has no influence upon the results of the analysis for phosphate if the alkalimetric procedure, based on precipitation as ammonium molybdophosphate, is used or if the molybdophosphate reaction is only utilized for the removal of interfering ions. Not surprisingly, therefore, the cation exchange phenomenon received little further attention.

MEIER and TREADWELL[5] studied the differences in solubility of various potassium, rubidium and caesium salts and calculated thermodynamically the maximum differences to be expected for the different alkali salts with large complex anions. The validity of the theory was tested for the alkali molybdophosphates by investigating by an equilibrium method the exchange of potassium, rubidium and caesium ions with the ammonium ions of the precipitate. The extent of exchange was found to be increasing in the order potassium, rubidium, caesium, and for each alkali ion to increase with increasing proportion of ammonium molybdophosphate used per equilibration. From the shape of the isotherms they concluded that the ion exchange probably took place by rapid adsorption on the surface of the particles until saturated, followed by a second phase of slow exchange into the interior of each particle, resulting in an approximately linear concentration gradient of the alkali ion between the surface and the centre of the particle.

NYDAHL has been reported by LINDQVIST[6] to have found ammonium molybdophosphate an efficient ion exchanger for the heavier alkali metal ions, but details of his work have apparently not been published.

In the course of this study a further paper on the cation exchange of ammonium molybdophosphate was published by BUCHWALD and THISTLETHWAITE.[7] They examined the ion exchange properties of this compound by treating suitable quantities of the solid with acidified solutions of the nitrates of Group I and Group II elements, as well as that of thallous thallium, and then analysing the precipitate and liquors. Their results indicate a high degree of exchange with K, Rb, Cs and Tl, but only insignificant exchange with Li, Na and Group II metal ions.

This is the first of a series of papers from this laboratory describing the results of a more detailed study of the ion exchange properties of the ammonium salts of a number of heteropolyacids. Some preliminary data for ammonium molybdophosphate have already been published.[8]

## EXPERIMENTAL

*Preparation of ammonium heteropolyacid salts*

Most of the salts were prepared by modifications of methods described by GRÜTTNER and JANDER.[9] Analytical grade reagents were used throughout, unless stated otherwise. As preparation of some heteropolyacid salts by different routes yielded materials with markedly different ion exchange properties, the methods used are described in full detail below.

1. *Ammonium molybdophosphate (AMP)*—(a) *Direct.* The citromolybdate procedure of KASSNER *et al.*[10] was modified in order to conserve expensive molybdate and at the same time to allow precipitation of large quantities of this compound in the presence of the desired excess of molybdate reagent.

[5] D. MEIER and W. D. TREADWELL, *Helv. Chim. Acta* **34**, 155 (1951).
[6] I. LINDQVIST, *Nova Acta Reg. Sci. Uppsala* **15**, (IV), No. 1 (1950).
[7] H. BUCHWALD and W. P. THISTLETHWAITE, *J. Inorg. Nucl. Chem.* **5**, 341 (1958).
[8] J. VAN R. SMIT, *Nature, Lond.* **181**, 1530 (1958).
[9] B. GRÜTTNER and G. JANDER, *Handbuch der Präparativen Anorganischen Chemie* (Edited by G. BRAUER), p. 1258. Ferdinand Enke Verlag, Stuttgart (1954).
[10] J. L. KASSNER, H. P. CRAMMER and M. A. OZIER, *Analyt. Chem.* **20**, 1052 (1948).

Eighty-one grammes of ammonium nitrate, 81 g of citric acid monohydrate and 102 g of ammoniumpar amolybdate $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ were dissolved in 2140 ml of water without heating. In a four-litre beaker, 456 ml of 60 per cent C.P. nitric acid were diluted with 390 ml of water and the citromolybdate solution slowly poured into the dilute acid, with stirring, to obtain a clear final solution.

A 10 ml solution of 0·5 g of diammonium hydrogen phosphate $(NH_4)_2HPO_4$ in water was then added to the acid-citromolybdate reagent, while stirring. The mixture was heated to boiling and maintained at the boiling point for about 2 min. ▱ After cooling for half an hour or longer, the precipitate was filtered through a Buchner funnel. The mother liquor was returned to the original beaker and the precipitate rinsed with 1 N ammonium nitrate solution into a separate container for further treatment subsequently.

Fifty millilitres of a solution containing 160 g/l. of ammonium paramolybdate were slowly added, with stirring, to the cooled mother liquor. Stirring continuously, 2.60 ml of 60 per cent nitric acid* were then added, followed by slow addition of a 10 ml aqueous solution of 0·5 g of diammonium hydrogen phosphate. The solution was then heated to boiling and filtered at the pump, as described above. The preparation was carried out in triplicate and the cycle repeated several times from ▱ for each until a total of about 400 g of AMP was obtained.

All the AMP was next slurried on to a Buchner funnel with 1 N ammonium nitrate and filtered with suction. The precipitate was now repeatedly washed with portions of 1 N ammonium nitrate until the pH of the washings was above 3·0. This was followed by washing with a few portions of 0·1 N ammonium nitrate. The precipitate was finally sucked well dry and was then exposed to the air for two to three days until a fine, dry, yellow powder was obtained. This was thoroughly mixed to ensure homogeneity, and stored in the dark in an air-tight container.

(b) *Via free acid.* Molybdophosphoric acid was prepared by boiling a mixture of 6·3 g of 25 per cent phosphoric acid in 100 ml of water and 35 g of molybdic oxide $MoO_3$ for 2 hr. The mixture was filtered and the filtrate cooled in ice to well below room temperature. Five millilitres of conc. hydrochloric acid were now added to the filtrate and the resulting solution extracted with several portions of ethyl ether. The oily co-ordination compound between the heteropolyacid and ether was collected in a wash bottle and 20 ml of distilled water added. The ether was removed by immersing the wash bottle in hot water and bubbling air for 30 min.

The resulting aqueous solution was diluted to 125 ml and AMP precipitated at room temperature by dropwise addition of 20 ml of 3 M ammonium nitrate solution. After standing overnight, the precipitate was filtered off, washed and dried as described above.

(c) *By "second precipitation".* If AMP is dissolved in a small excess of ammonia and molybdate and ammonium nitrate added to the solution, the precipitate may be formed again by acidification. It has been found[12] that if the conditions for this "second precipitation" are such that the molybdate, ammonium and nitric acid concentration and temperature of precipitation are identical with those of the "first precipitation", the "second precipitation" is much more rapid and complete than the "first precipitation" and the AMP is usually obtained in a finer form. AMP prepared in this way has therefore been considered separately.

A small quantity of AMP was prepared by such a "second precipitation", choosing a final molybdate, phosphate and ammonium ion concentration identical with that in the classical method for precipitating AMP, as described by VOGEL[13]. After allowing to stand for 2 hr, the precipitate was filtered, washed with 0·1 N ammonium nitrate, and air-dried.

The material obtained by each of these methods was bright yellow.

2. *Ammonium molybdoarsenate (AMA)*—(a) *Direct.* One gramme of arsenious oxide $As_2O_3$ was dissolved in the minimum amount of hot 60 per cent C.P. nitric acid* and the resulting solution

* It has been shown[11] that the molybdate species taking part in the molybdophosphate reaction is probably the paramolybdate ion $Mo_7O_{24}^{6-}$, rather than orthomolybdate $MoO_4^{2-}$, as suggested by most textbooks. This quantity of acid then represents the amount of nitric acid consumed when 0·5 g of $(NH_4)_2HPO_4$ takes part in the reaction:

$$12(NH_4)_6Mo_7O_{24} + 7(NH_4)_2HPO_4 + 65HNO_3 \longrightarrow 7(NH_4)_3PMo_{12}O_{40} + 36H_2O + 65NH_4NO_3$$

* The $As^{III}$ is simultaneously oxidized to $As^{V}$ during this operation.

(11) A. GRAY, M.Sc. Thesis, University of Stellenbosch (1954); G. JANDER and K. F. JAHR, *Kolloid-Beih.* **41**, 297 (1935).

(12) J. VAN R. SMIT, M.Sc. Thesis, University of Stellenbosch (1953).

(13) A. I. VOGEL, *A Text-book of Quantitative Inorganic Analysis* p. 464. Longmans, Green, London (1948).



Vol. 12 59/60

added to a 1 l. solution containing 120 g of ammonium nitrate. One-and-a-half litres of acid-molybdate reagent were prepared according to the directions of Vogel.[13] Both solutions were heated to 40°C and the molybdate reagent added to the arsenate solution. A pale yellow precipitate formed very slowly. It was filtered off after two days standing, washed with 0·1 N ammonium nitrate solution and dried in the air.

(b) *Via sodium salt.* Four grammes of arsenious oxide were dissolved in the minimum quantity of hot nitric acid and the solution added to a solution of 30 g of sodium molybdate $Na_2MoO_4 \cdot 2H_2O$ in 150 ml of water. The mixture was neutralized and made about 1 N in acid by the addition of conc. hydrochloric acid. The ammonium salt was precipitated at 45°C by dropwise addition of excess of saturated ammonium chloride. After several hours the precipitate was filtered off, washed and air-dried as described. The product obtained was light grey in colour.

(c) *Via free acid.* A solution of 25 g of sodium molybdate in 100 ml of water was carefully added to 6 ml of 60 per cent nitric acid to obtain a clear solution. In the minimum amount of nitric acid 0·8 g of arsenious oxide was dissolved and the solution added to the acid molybdate solution. Five millilitres of conc. hydrochloric acid were added, the solution cooled in ice, and extracted with 5 ml of ether, collecting the lower oily layer in a wash bottle. The extraction was repeated several times with 5 ml portions of ether after the addition of 2 ml quantities of conc. hydrochloric acid, until no further amounts of the oily compound were formed.

A small amount of water was now added to the wash bottle and the ether removed as described under 1(b). The final solution was diluted to 100 ml and AMA precipitated at room temperature by the slow addition of 20 ml of 3 M ammonium nitrate. Filtration, washing and drying of the precipitate were carried out as for the other preparations. The product obtained was bright yellow, closely resembling AMP.

3. *Ammonium molybdosilicate (AMS).* A small amount of laboratory reagent quality sodium silicate (water glass) and two pellets of sodium hydroxide were dissolved in 20 ml of water and boiled for 15 min in order to convert all the silicate to the monomer. After cooling, the solution was added to a molybdate solution containing 25 g of sodium molybdate in 100 ml of water. The mixture was now neutralized to a pH of about 1·5 by dropwise addition of 1:1 nitric acid.

After filtering, 2 ml of conc. hydrochloric acid were added and molybdosilicic acid extracted with several portions of ether, with the addition of 2 ml quantities of conc. hydrochloric acid before each equilibration. The ether-heteropolyacid compound was received in a wash bottle, water added, and the ether removed as previously described. The solution was now diluted to 100 ml and the white ammonium molybdosilicate precipitated by slow addition of an excess of saturated ammonium chloride.

4. *Ammonium tungstophosphate (AWP)*—(a) *Via sodium salt.* A solution containing 50 g of sodium tungstate $Na_2WO_4 \cdot 2H_2O$ and 25 g of disodium hydrogen phosphate $Na_2HPO_4 \cdot 12H_2O$ in about 100 ml of water was evaporated at 80°C until crystals started to form. To this were carefully added 75 ml of 24 per cent hydrochloric acid and the solution again evaporated at this temperature until crystals started to form. The solution was then diluted twofold and AWP obtained by dropwise addition of an excess of a saturated solution of ammonium chloride. This was followed by the usual filtration, washing with 0·1 N ammonium nitrate, and drying in the air.

(b) *Via free acid.* A solution containg 25 g of sodium tungstate and 0·8 g of phosphoric acid, specific gravity 1·70, in 40 ml of water was prepared. To this was slowly added 40 ml of 24 per cent hydrochloric acid, with stirring. The solution was cooled down in ice water, 5 ml of conc. hydrochloric acid added, and then extracted with small portions of ethyl ether, adding 2 ml amounts of conc. hydrochloric acid before each equilibration. Further treatment of the ether–heteropolyacid compound to prepare AWP was identical with that described for AMS. A white, microcrystalline material was obtained.

5. *Ammonium tungstoarsenate (AWA)*—(a) *Via free acid.* One gramme of arsenious oxide was dissolved in the minimum quantity of hot conc. nitric acid and the resultant solution carefully added to a solution of 25 g of sodium tungstate in water. The acidity was then adjusted to about 0·1 M in nitric acid. The solution was heated to 60°–70°C and kept at this temperature for a few minutes. This was followed by the addition of 20 ml of conc. hydrochloric acid, cooling in ice, and extraction with ether as described for AMS.

From the extract an aqueous solution was prepared in the usual manner, AWA precipitated with saturated ammonium chloride solution, followed by filtering, washing and drying, as described. The material obtained was light yellow.

Vol. 12 1959/6

(b) *Via sodium salt.* A solution containing 43 g of sodium tungstate in 100 ml of water was added to a solution containing 3 g of arsenious oxide, dissolved in conc. nitric acid. The solution was made strongly acidic by neutralizing with conc. hydrochloric acid and adding 5 ml in excess. The ammonium salt was now prepared by dropwise addition of saturated ammonium chloride solution. Filtering, washing and drying were then performed in the usual manner. A cream-coloured compound was obtained.

6. *Ammonium tungstosilicate (AWS).* This was prepared in the same way as AMS, using 30 g of sodium tungstate and a small amount of sodium silicate as starting materials. The final AWS product was white.

7. 8-*Hydroxyquinoline molybdophosphate (QMP).* A small quantity of this compound was prepared according to the directions of GOTTSCHALK.[14]

*Distribution coefficients*

Batch distribution coefficients were determined by agitating weighed amounts (usually about 0·25 g) of the ion exchanger with 15 ml of 0·1 N ammonium nitrate, containing a trace quantity of the element in question, overnight in a thermostat bath at 25 ± 0·2°C. This was followed by filtration of the mixture through Whatman No. 40 filter paper and analysis of the filtrate. In some cases a clear filtrate could only be obtained after repeated filtration, while in others formation of a colloidal solution prevented the determination of distribution coefficients.

Distribution coefficients were calculated by means of the usual relationship

$$K_d = \frac{\text{Concentration of X per gramme of exchanger}}{\text{Concentration of X per ml of solution}}$$

where X is the ionic species in question.

The radiotracers $^{24}Na$, $^{42}K$, $^{86}Rb$, $^{204}Tl$, $^{110}Ag$ (compounds or metals irradiated in the Harwell pile) and $^{137}Cs$ (obtained from the Radiochemical Centre, Amersham) were used for measuring relative concentrations.

## RESULTS AND DISCUSSION

Distribution coefficients were determined for the alkali metals (except for lithium) and, in the case of AMP, also for thallium (I) and silver. Mercury (I) should also exchange with AMP, but was not included in this study. For the purpose of comparison, distribution coefficients for the alkali metals have also been determined with air-dried Dowex 50 in the ammonium form. In each case the acidity of the solution before equilibration was adjusted with nitric acid to a pH of 2·0 ± 0·1. The pH after equilibration was always found to have changed by not more than 0·1 pH units.

As already stated, some of the preparations were too fine to allow separation of the liquid and solid phases by filtration or centrifugation. The 0·25 g quantities of AMS and AWS were found to have dissolved completely in the 15 ml of 0·1 N ammonium nitrate solution after equilibration overnight, and $K_d$ values could therefore not be obtained for them.

Examination of the results, summarized in Table 1, shows the adsorbabilities of the alkali metals for a particular heteropolyacid salt to increase with increasing atomic number, or size, of the alkali metal, as with "strong-base" organic exchangers. The same is true for silver and thallium, for which the $K_d$ values for AMP are higher than for the alkali ions of corresponding size. This is probably due to the partial covalent character of the bonds between thallium or silver ions and the molybdophosphate anion, which has the effect of increasing the effective size of the cation.

The separation factors for pairs of alkali metals (defined as the ratio of their distribution coefficients under similar experimental conditions) are seen to be more

[14] G. GOTTSCHALK, *Z. Anal. Chem.* **158**, 257 (1958).

TABLE 1.—DISTRIBUTION COEFFICIENTS OF VARIOUS CATIONS WITH THE AMMONIUM HETEROPOLYACID SALTS IN 0·1N AMMONIUM NITRATE SOLUTION

(For the meaning of abbreviations, see text.)

| Ion exchanger | Method of preparation | Distribution coefficient, $K_d$(ml/g) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cs | | | Rb | | | K | | | Na | Tl | | Ag | |
| AMP | Direct | 5515 | 5553 | 5443 | 191 | 193 | 193 | 3·0 | – | 5·0[a] | ~0 | 4240 | 4350 | 26·6 | 25·2 |
| AMP | Via free acid | 5583 | 5489 | 5626 | | – | | | | | | | | | |
| AMA | Direct | 697 | 690 | | 124 | 125 | | 20 | | 19 | ~0 | | | | |
| AMA | Via free acid | 4180[b] | | 1186[c] | 188[b] | | 63·4[c] | 4·7[b] | | 6·4[b] | ~0 | | | | |
| | | 4130[b] | | 1169[c] | 186[b] | | 61·9[c] | | | | | | | | |
| AMA | Via sodium salt | 373, | 381 | | | | | 32·5 | | 33·3 | ~0 | | | | |
| AWP | Via free acid | 3950[b] | | 3243[c] | 134[c] | | | | | | | | | | |
| | | 4140[b] | 3256[c] | 3318[c] | 134[c] | | | | | | | | | | |
| AWP | Via sodium salt | 3510, | 3480 | | 136, | 136 | | 5·4 | | 4·6 | ~0 | | | | |
| AWA | Via sodium salt | [d] | | | | | | | | | | | | | |
| AWA | Via free acid | [d] | | | | | | | | | | | | | |
| AWS | Via free acid | [e] | | | | | | | | | | | | | |
| AMS | Via free acid | [e] | | | | | | | | | | | | | |
| QMP | Direct | 1499 | 1510 | | | | | | | | | | | | |
| Dowex 50, $NH_4$-form | – | 62 | | | 52 | | | 46 | | | 26 | | | | |
| Crystallographic radius [f] | | 1·69 | | | 1·48 | | | 1·33 | | | 0·95 | 1·44 | | 1·26 | |

[a] Reproducibility only moderate.
[b] Determined on material prepared by W. R.
[c] Determined on material prepared by J. J. J.
[d] Formed colloidal solution
[e] Dissolved completely.
[f] According to WELLS,[22] Ionic radius for $NH_4^+$ given as 1·48.

Vol. 12 1959/60

than ten times as high for some of the ammonium heteropolyacid salts as for Dowex 50. This allows for much more efficient separation of the alkali metals on a column of the ammonium heteropolyacid salts than for columns of synthetic organic resins,[15,16] as has already been demonstrated for AMP.[8] A more detailed account of the separation of the alkali metals on columns of AMP is given in a subsequent paper.[17]

If only a trace amount of the ion whose distribution coefficient is being determined is involved, $K_d$ may be expected to be almost independent of the weight of ion exchanger taken, as long as the loading does not exceed about 1 per cent. Table 2 shows

TABLE 2.—VARIATION OF THE DISTRIBUTION COEFFICIENT OF CAESIUM IN 0·1 N AMMONIUM NITRATE SOLUTION WITH THE WEIGHT OF AMA USED IN THE EQUILIBRATION

| Weight of AMA taken (g) | 0·2498 | 0·2506 | 0·1005 | 0·2504 | 0·2498 | 0·1005 | 0·0998 |
|---|---|---|---|---|---|---|---|
| $K_d$ | 1197 | 1186 | 2054 | 1167 | 1169 | 2029 | 2076 |

that this is not true for the exchange of caesium on AMA in dilute ammonium nitrate solution. Further investigation is required before this phenomenon can be explained.

## NATURE OF THE ION EXCHANGE ON THE AMMONIUM HETEROPOLYACID SALTS

There is little doubt that AMP and the other heteropolyacid salts owe their cation exchange properties and high selectivity for monovalent ions to their peculiar crystal structure, and it seems appropriate to consider briefly the structure of this class of compounds, using AMP as an example.

AMP is the insoluble ammonium salt of a member of a group of complex acids formed by the oxides of molybdenum and tungsten with phosphoric or arsenic acid, called the 12-heteropolyacids. The general formula of these acids may be written as $H_3XY_{12}O_{40} \cdot nH_2O$ where X is P or As and Y is Mo or W.

X-ray studies of the heteropolyacids[18,19] and their salts,[20,21] summarized by WELLS,[22] have shown that a heteropolyacid anion, such as molybdophosphate, consists of a hollow sphere formed by the twelve linked $MoO_6$ octahedra, with the $PO_4$ group in the centre. In crystals of the salts, the cations with associated water molecules are fitted in between these spheres of relatively large negative ions. Comparatively large interspaces or "cavities" exist between these spheres, allowing for the accommodation of large cations, even cations as large as the organic bases strychnine, 8-hydroxyquinoline, etc. Apart from ammonium ions, only the large monovalent cations, viz. $K^+$, $Rb^+$, $Cs^+$, $Tl^+$, $Ag^+$, $Hg^+$ and organic bases are sufficiently large to be packed stably enough into this structure to lower the crystal energy sufficiently to give salts insoluble in water.

[15] G. KAYAS, *J. Chim. Phys.* **47**, 408 (1950).
[16] S. A. RING, *Analyt. Chem.* **28**, 1200 (1956).
[17] J. VAN R. SMIT, W. ROBB and J. J. JACOBS, *J. Inorg. Nucl. Chem.* **12**, 104 (1959).
[18] J. F. KEGGIN, *Proc. Roy. Soc.* A **144**, 75 (1934).
[19] A. J. BRADLEY and J. W. ILLINGWORTH, *Proc. Roy. Soc.* A **157**, 113 (1936).
[20] J. W. ILLINGWORTH and J. F. KEGGIN, *J. Chem. Soc.* 575 (1935).
[21] J. A. SANTOS, *Proc. Roy. Soc.* A **150**, 309 (1935)
[22] A. F. WELLS, *Structural Inorganic Chemistry* (2nd Ed.), pp. 348–55. Clarenden Press, Oxford (1950)

These inorganic ions are the only ions that exchange in acidic medium with the ammonium ions on the ammonium heteropolyacid salts, for the cavities and the channels linking neighbouring cavities in these crystals are large enough to allow free movement of the inorganic cations about in the crystal. The cations may also move in and out of the lattice and be reversibly exchanged for other cations. In view of the porous structure of these salts, the ion exchange should therefore take place throughout the entire crystal lattice and not only on the surface of the crystals as previously thought.[5]

With salts of the heteropolyacids with organic bases, such as 8-hydroxyquinoline, the ion exchange may be expected to take place on the surface only, for, although the cations of 8-hydroxyquinoline still fit comfortably into the cavities between the heteropolyanions, they are too large to pass through the channels linking neighbouring cavities, and therefore cannot move about in the crystal lattice or out of it.

This is substantiated by experiment. When tracer caesium was shaken overnight in 0·1 N ammonium nitrate solution with QMP, a distribution coefficient of about 1,500 was found (Table 1). The caesium was probably adsorbed by ion exchange on the surface or by incorporation in the QMP structure during slow recrystallization of the compound. However, unlike with AMP, the tracer caesium, when applied to the top of a column of QMP, followed immediately by elution with dilute ammonium nitrate solution, was not adsorbed, but more than 99 per cent of it came off with the first few column volumes. This shows that salts of organic bases and the heteropolyacids are unsuitable as ion exchange materials.

## ION EXCHANGE OF THE AMMONIUM HETEROPOLYACID SALTS PREPARED BY DIFFERENT ROUTES

Samples of AMP gave similar distribution coefficients, within experimental error, whether prepared directly or via the free acid (Table 1). This was not true for AWP and AMA, notably for the latter, where large differences in $K_d$ values were found for the materials prepared directly, via the sodium salt, or via the free acid. These different materials were also different in physical appearance, especially in colour.

These differences were thought to be due to differences in crystal structure of the different materials. X-ray diffraction patterns of the various materials were obtained using a Philips diffractometer (Co $K\alpha$ radiation, Fe filter, maximum $2\theta = 60°$). The different preparations of AMA were found to contain three different components, as shown in Table 3. Component C is probably the one responsible for the

TABLE 3.—DIFFERENT CRYSTALLOGRAPHIC COMPONENTS IN AMMONIUM HETEROPOLYACID SALTS PREPARED BY DIFFERENT ROUTES

| Sample | Method of preparation | | | |
|---|---|---|---|---|
| | Direct | Via sodium salt | Via free acid | By second precipitation |
| AMA | A | B | A + C* | — |
| AMP | A + C† | — | C | C |

* About 60 per cent of C. † More than 95 per cent of C.

high selectivity for the alkali ions, as AMP, which has the highest selectivity of the materials studied, consists almost entirely of this component. This crystallographic component is probably the same as that found by ILLINGWORTH and KEGGIN.[20]

The X-ray diffraction pattern of AMS was also obtained. This was found to differ markedly from the patterns found with AMA and AMP. None of the three crystallographic components found in the different preparations of AMA and AMP were present in the AMS sample.

## INFLUENCE OF pH ON DISTRIBUTION COEFFICIENTS

A number of determinations of $K_d$ for rubidium in 0·1 N ammonium nitrate solution with AMP was carried out using solutions of different pH values. The pH values recorded were those measured after equilibration. As might be expected, the $K_d$ values (Table 4) were constant, within experimental error, over the pH range studied.

TABLE 4.—INFLUENCE OF pH ON THE DISTRIBUTION COEFFICIENT OF RUBIDIUM WITH AMP IN 0·1 N AMMONIUM NITRATE

| pH of solution | 1·15 | 2·15 | 3·65 | 4·50 |
|---|---|---|---|---|
| $K_d$ | 192 | 190 | 191 | 186 |

Adsorbabilities of other alkali ions from dilute ammonium nitrate solutions are probably also independent of pH over this range (1·2–4·5).

Multivalent ions do not exchange significantly in acid solution, but are strongly adsorbed from neutral solution (pH 2·5–5·0), their adsorbability being highly dependent on the pH of the solution. This is dealt with in a separate paper.[23]

*Acknowledgement*—We are indebted to Dr. F. HERBSTEIN and his group for the X-ray analyses. This paper is published by permission of the South African Council for Scientific and Industrial Research.

[23] J. VAN R. SMIT and W. ROBB. To be published.

Vol. 12 59/60

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 104 to 112. Pergamon Press Ltd. Printed in Great Britain.

# CATION EXCHANGE ON AMMONIUM MOLYBDOPHOSPHATE—I

## THE ALKALI METALS

J. VAN R. SMIT, W. ROBB and J. J. JACOBS

National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, Pretoria

(*Received* 23 *February* 1959; *in revised form* 25 *April* 1959)

**Abstract**—The use of ammonium molybdophosphate (AMP) as a cation exchanger for the chromatographic separation of alkali metals has been investigated. This material is only obtained as very fine crystals, but large columns with favourable flow rates may be prepared from mixtures of AMP and asbestos. The feasibility of separating the alkali metals, sodium, potassium, rubidium and caesium, from one another on columns of AMP-asbestos has been demonstrated. These separations can be performed more efficiently than with columns of conventional organic ion exchangers. In the separation of pairs of alkali ions a small amount of the more strongly adsorbed alkali can be selectively adsorbed from solutions containing quantities of the more weakly adsorbed ion representing up to several times the maximum loading capacity of the column.

The mass action law has been shown to apply to the exchange between rubidium and ammonium ions on AMP. Breakthrough curves for the rubidium–ammonium and caesium–ammonium exchange on AMP resemble those obtained with "strong-base" organic resins. The saturation exchange capacity of AMP for rubidium and caesium is only about two-thirds of the theoretical figure, calculated from the known composition of AMP and assuming that all its ammonium ions are exchangeable.

Vol
12
1959/

IN the preceding paper[1] we have reported on the cation exchange properties of the ammonium heteropolyacid salts. It was shown by equilibrium experiments that the various alkali metal ions are adsorbed on to these salts by exchange and that the adsorbability of the various alkali ions is greater the larger their relative crystallographic radii. Thus, in 0·1 N ammonium nitrate solution, sodium shows negligible exchange, while caesium is very strongly adsorbed.

This paper describes the application of the cation exchange properties of the heteropolyacid salts to the chromatographic separation of alkali metal ions on columns of these materials. Although some other heteropolyacid salts, such as ammonium tungstophosphate and ammonium molybdoarsenate, may also be used successfully for column separations, we have confined our investigation to ammonium molybdophosphate (AMP) as this compound shows the highest selectivity for the alkali metals and is the best known and cheapest of the ammonium heteropolyacid salts. It is also easily prepared in large quantities and hence is anticipated to find more ready application as an ion exchange material than the other heteropolyacid salts. The feasibility of separating trace amounts of the alkali metals on a column of AMP has already been demonstrated in an earlier report;[2] the work has now been extended to the separation of macro quantities of the alkali metals.

[1] J. VAN R. SMIT, J. J. JACOBS and W. ROBB, *J. Inorg. Nucl. Chem.* **12**, 95 (1959).
[2] J. VAN R. SMIT, *Nature, Lond.* **181**, 1530 (1958).

## USE OF LARGE COLUMNS OF AMP

The same batch of material used in previous experiments[1] has been used here. This was prepared by an adaption of the citromolybdate procedure for the precipitation of AMP of KASSNER *et al.*[3]

AMP, as well as other insoluble heteropolyacid salts, always precipitates out as a microcrystalline product. With column beds of AMP suitable for separating weighable amounts of the alkali metal ions, a workable flow rate would therefore be extremely difficult to obtain.

Efforts to obtain large crystals of AMP, or to convert them into a granular form without the aid of a binder, have met with little success. The tendency of the insoluble heteropolyacid salts to form only very fine crystals may perhaps be attributed to the weak crystal forces resulting from their peculiar structure. It may be recalled that free heteropolyacids, as well as their soluble salts, crystallize out from aqueous solutions as well-developed large crystals with large numbers of water molecules of crystallization. When these are left to dry in the air, they lose water and break down into the pentahydrates, which have a microcrystalline character resembling the insoluble heteropolyacid salts both in appearance and in crystal structure.[4,5] In the freshly crystallized material the water of hydration is responsible for cohesion and permits the existence of large crystals, but in the pentahydrate structure the presence of fewer molecules of water apparently only provides for greatly diminished cohesion, with the formation of only very fine crystals. Hence, even if large crystals were to be prepared they would probably disintegrate into smaller particles when brought into contact with water or aqueous solutions.

Vol. 12 59/60

This problem, it has now been found, is easily overcome, by employing mixtures of AMP with asbestos, such as the material used for Gooch crucibles. When these two are mixed in water or an electrolyte solution (e.g. in a 1 : 1 ratio, by weight), the AMP crystals appear to adhere firmly to the asbestos fibres, and when the mixture is allowed to settle, the two show no tendency to separate. When the mixture is poured into a column, the AMP–asbestos mixture packs well into a bed, with no apparent separation or non-uniformity. Large columns of AMP–asbestos may be prepared in this way with very favourable flow rates. As the average particle size of the AMP (usually substantially smaller than 200 mesh) cannot be readily controlled, the flow rate may be altered by changing the ratio of asbestos to AMP.

AMP–asbestos columns have the advantage that they may be allowed to "run dry" with little danger of air bubbles entering the column bed.

## PREVIOUS METHODS OF SEPARATING THE ALKALI METAL IONS

In many methods of analysis for particular alkali metal ions, other alkalis frequently interfere seriously. This is particularly true for the heavier alkalis. For instance, precipitation reactions with potassium which form the basis of methods of determining this element, such as the tetraphenyl borate,[6] molybdosphosphate,[7] perchlorate methods, etc., are also given by rubidium and caesium. Although there are

[3] J. L. KASSNER, H. P. CRAMMER and M. A. OZIER, *Analyt. Chem.* **20**, 1052 (1948).
[4] J. A. SANTOS, *Proc. Roy. Soc.* A **150**, 309 (1935).
[5] J. W. ILLINGWORTH and J. F. KEGGIN, *J. Chem. Soc.* 575 (1935).
[6] W. LIEBER, *Zement-Kalk-Gips* **10**, 61 (1957) and further references given therein.
[7] R. BELCHER and J. W. ROBINSON, *Anal. Chim. Acta* **8**, 239 (1953).

suitable precipitation methods, such as the tungstosilicate procedure,[8] for separating potassium and caesium, the available methods for the separation of potassium and rubidium are less satisfactory. There is even a greater paucity of methods for the separation of caesium and rubidium, other than by chromatography, especially when these are present in trace quantities. Chromatographic methods include the cation exchange methods of KAYAS,[9] RING[10] and DAVIES and OWEN[11], utilizing conventional organic resins, an ion exchange method utilizing complexing agents,[12] paper chromatography[13] and the recently developed cation exchange on synthetic inorganic exchangers.[14–16] With the exception of the latter, these methods are lengthy and cumbersome, and separation factors for pairs of neighbouring alkali metals are rather unfavourable.

## SEPARATION OF THE ALKALI METAL IONS ON COLUMNS OF AMP–ASBESTOS

*Experimental methods*

In the separation experiments described in this section, the AMP–asbestos columns were prepared by weighing out the desired quantities of the materials in one container and adding sufficient 0·1 N ammonium nitrate to allow thorough mixing. After mixing, the slurry was poured into a glass column, using glass-wool and some asbestos as a column support. The mixture was then allowed to settle while the column drained. When weakly adsorbed ions (e.g. sodium and potassium) were to be separated, the column was first conditioned by passing through 0.01 N ammonium nitrate. With more strongly retained ions this was unnecessary, and the column was ready for use as soon as the liquid used for the packing of the column was drained off.

The nuclides $^{24}Na$, $^{42}K$, $^{86}Rb$ (obtained from A.E.R.E., Harwell) and $^{137}Cs$ (supplied by the Radiochemical Centre, Amersham) were employed for measuring relative concentrations. In some of the experiments, effluent fractions of a few drops each were collected in test tubes and the elution curve obtained by measuring the radioactivity of each fraction. In other cases (e.g. in the separation of potassium and rubidium) the effluent activity was measured by passing the column effluent through a G.M. flow-counter, connected to a count-rate meter, and reading off the effluent activity at suitable intervals.

*Separation of sodium and potassium.* The separation of 1·3 mg of sodium and 2·03 mg of potassium on a 2 : 1 column of AMP–asbestos is shown in Fig. 1a. These quantities represent a maximum column loading of about 2·5 per cent with respect to sodium and about 2·3 per cent with respect to potassium, assuming an exchange capacity of 1·57 m-eq/g of AMP for each (see later). This figure is obviously too high, as the trisodium salt of molybdophosphoric acid is very soluble in water, and the corresponding potassium salt, while still reasonably insoluble, is appreciably more soluble than AMP. It may safely be assumed, therefore, that only a fraction of the ammonium ions in AMP are available for exchange with sodium ions. Hence, the actual exchange capacity of AMP for sodium should be far below that of the theoretical figure. This explains the form of the sodium peak which indicates that only part of the sodium had actually been retained by the AMP, while the rest passed through unretarded. The remarkable selectivity of AMP for the alkali metals is borne out by Fig. 1b. This shows the separation of 104 mg of sodium from 1·02 mg of potassium, corresponding to about

[8] W. W. SCOTT, *Standard Methods of Chemical Analysis* (5th Ed.), p. 897. Van Nostrand, New York (1945).
[9] G. KAYAS, *J. Chim. Phys.* **47**, 408 (1950).
[10] S. A. RING, *Analyt. Chem.* **28**, 1200 (1956).
[11] C. W. DAVIES and B. D. R. OWEN, *J. Chem. Soc.* 1676 (1956).
[12] F. NELSON, *J. Amer. Chem. Soc.* **77**, 813 (1955).
[13] For example see A. E. STEEL, *Nature, Lond.* **173**, 316 (1954).
[14] K. A. KRAUS, H. O. PHILLIPS, T. A. CARLSON and J. S. JOHNSON, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, P/1832.
[15] E. A. C. CROUCH, J. A. CORBETT and H. H. WILLIS, AERE C/R-2325 (1957).
[16] C. B. AMPHLETT, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, P/271

200 and 1 per cent column loading, respectively. There is no other method of separation, whether by ion exchange or otherwise, capable of separating similar quantities of these two alkali metals as simply, rapidly and as efficiently.

*Separation of potassium and rubidium.* The separation of small quantities (e.g. 2 mg) of potassium and rubidium has been carried out successfully with a column of the same dimensions as that used for the sodium–potassium separation. More concentrated elutriants were employed in this separation. Fig. 2 shows the selective adsorption of 19 mg of rubidium (representing a column loading of about

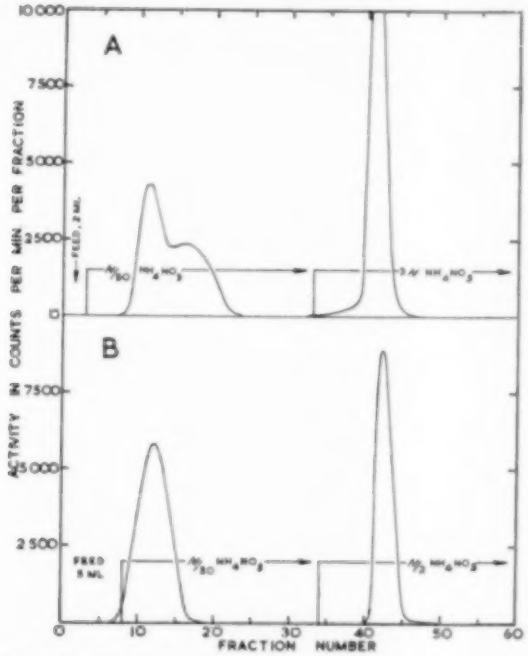



FIG. 1A:—Separation of 1·3 mg of Na and 2·03 mg of K.
Column: 1·48 g of AMP + 0·74 g of asbestos.
Dimensions: 0·81 cm² × 6·8 cm.
B:—Separation of 104 mg of Na and 1·02 mg of K on same column as with A.

15 per cent) from a solution containing 600 mg of potassium. This quantity of potassium is about ten times the total maximum (theoretical) exchange capacity of the column.

*Separation of rubidium and caesium.* A column of AMP–asbestos has also been used for the separation of macroquantities of rubidium and caesium, as illustrated by Fig. 3. The method is suitable for the production of pure caesium and rubidium compounds in industry[17] and may be adapted for the separation and isolation of $^{137}Cs$ from fission product solutions.[17, 18] It may also be used for the concentration and separation of rubidium and caesium in a procedure for determining these two elements when present together.[19]

*Other separations.* Although the separation of other combinations of the alkali metal ions has not been investigated, it is clear that such separations should offer no difficulties. The selectivity of AMP for the larger alkali metals is such that small quantities of the larger alkali ions (such as caesium and rubidium) may always be selectively adsorbed from solutions containing large quantities of smaller alkali ions.

[17] J. VAN R. SMIT, Brit. Pat. Appl. No. 2787/59.
[18] J. VAN R. SMIT, W. ROBB and J. J. JACOBS, *Nucleonics* **17**, 116 (1959).
[19] J. VAN R. SMIT *et al.*, to be published.

Vol. 12 59/60

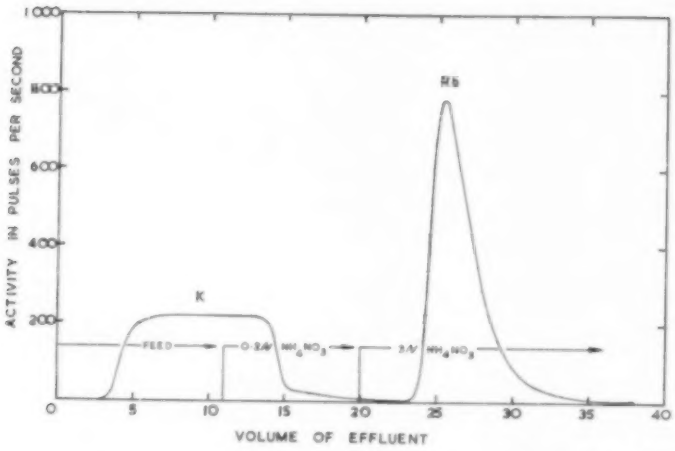



FIG. 2.—Separation of 600 mg of K from 19 mg of Rb.
Column: 1 g of AMP + 0·5 g of asbestos,
0·81 $cm^2$ × 3·3 cm.
Linear flow rate: ~ 1 cm/min.

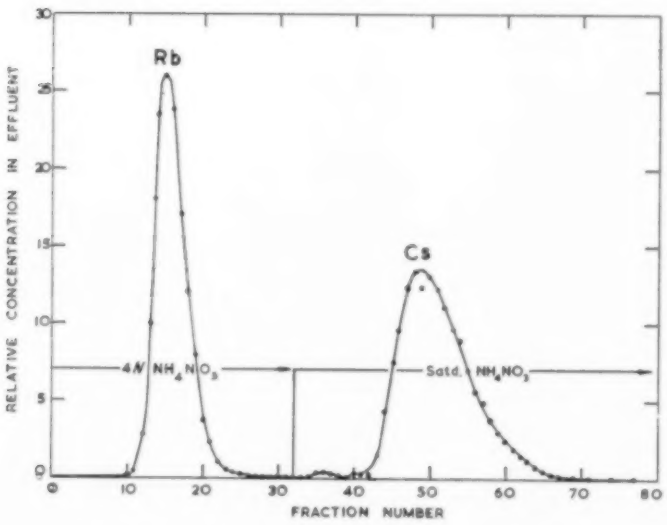



FIG. 3.—Separation of 12·3 mg of Rb and 13·5 mg of Cs.
Column: 50 : 50 (w/w) of AMP–asbestos,
1·54 $cm^2$ × 8·9 cm.
Each fraction of effluent = 10 drops.

In acidic solutions, only the relatively large monovalent ions, viz. $K^+$, $Rb^+$, $Cs^+$, $Ag^+$, $Hg^+$, and $Tl^+$, exchange significantly. These are the only ions that form molybdophosphates which are insoluble in aqueous systems.[7] This permits selective adsorption of these ions from solutions containing large quantities of multivalent ions or the relatively small monovalent ions, as the presence of these ions has only a small influence on the adsorbabilities on AMP of the strongly adsorbable ions.

For instance, tracer caesium may be quantitatively adsorbed from 20 l. of sea water on a column consisting of only 2 g each of AMP and asbestos. This extremely high selectivity of AMP for caesium may be used for determining $^{137}Cs$ fall-out in samples of rain, sea-water or river water.[20]

## MASS ACTION LAW APPLIED TO ION EXCHANGE ON AMP

The ion exchange between the alkali metal ions and the ammonium ions on AMP may be represented by the following equation (using the exchange with rubidium as an example):

$$Rb^+ + R\ NH_4 \rightleftharpoons Rb\ R + NH_4^+$$

where R represents the anionic molybdophosphate framework. In the mass action expression for this equilibrium,

$$K = \frac{[RbR][NH_4^+]}{[Rb^+][RNH_4]},$$

the term $[Rb\ R]/[Rb^+] = K_d$, the distribution coefficient, and, if only trace quantities of Rb are involved, $[R\ NH_4]$ may be taken as constant. The expression may then be written

$$K = K_d \times \frac{[NH_4^+]}{\text{constant}}$$

or

$$\log K_d = \text{constant} - \log [NH_4^+]$$

The variation of $\log K_d$ with $\log [NH_4^+]$ was determined for rubidium and, as may be seen from Fig. 4, the experimental points lie on a straight line of slope $= -1$ for the concentration range 0·05 M to 1·5 M, showing the ion exchange between rubidium and ammonium ions on AMP to obey the mass action law.

Fig. 4 also shows the variation of $K_d$ of rubidium in 0·1 N ammonium nitrate solutions containing varying quantities of lithium nitrate. The decrease in $K_d$ appears not to be the result of a true ion exchange reaction, but may possibly be ascribed to variations in the activity coefficients of the rubidium and ammonium ions in the two phases due to the presence of lithium nitrate.

## BREAKTHROUGH CURVES

Breakthrough curves for the caesium–ammonium and rubidium–ammonium exchange have been determined by passing a tagged caesium or rubidium solution of known concentration through a column bed consisting of 1 g each of AMP and asbestos. Fig. 5 shows these breakthrough curves to be reasonably symmetrical and to be analogous to those obtained with "strong-base" organic resins.[21] The symmetry of these curves, as well as that of the elution peaks in the separation experiments, where linear flow rates of about 1cm/min were maintained, shows the column to have operated under equilibrium conditions.

[20] J. VAN R. SMIT, W. R. MCMURRAY and J. J. JACOBS, to be published.
[21] For examples see O. SAMUELSON, *Ion Exchangers in Analytical Chemistry* Chap. V. John Wiley, New York (1953).

Vol. 12 59/60

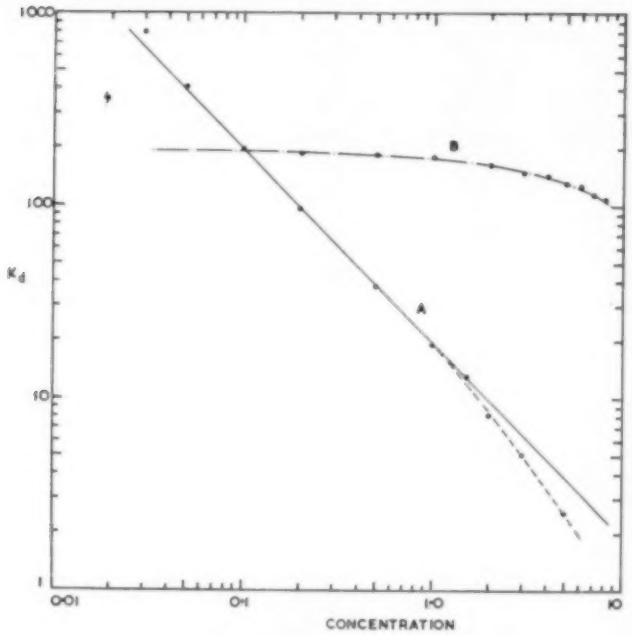



FIG. 4.—Variation of $K_d$ for Rb with concentration—
A. with $NH_4^+$ concentration, B. with $Li^+$ concentration.
(In the latter case, each solution also contained 0·1 mole of $NH_4NO_3$ per litre.)

Vol.
12
1959/6

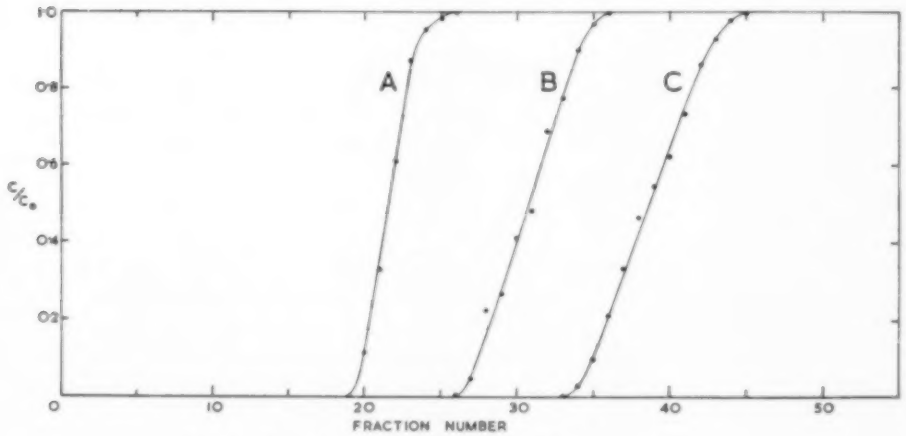



FIG. 5.—Breakthrough curves for Rb and Cs
1 g of AMP + 1 g of asbestos used in each run.
Column: 1 $cm^2$ × 7·4 cm.
A. With Cs solution containing 496 mg Cs/100 ml.
B. With Cs solution containing 311 mg Cs/100 ml.
C. With Rb solution containing 160 mg Rb/100 ml.

The influence of higher flow rates on the shape of the elution peaks or breakthrough curves has not been investigated, but it seems likely that linear flow rates considerably higher than 1 cm/min may be tolerated, since this is true in beds of synthetic organic exchangers. There is no reason to suspect that diffusion rates in AMP should be slower than in organic exchangers, and, in addition, the relatively small size of the AMP crystals would actually favour higher rates of exchange, and hence higher flow rates in AMP–asbestos columns.

TABLE 1.—NUMBER OF EQUIVALENTS OF AMMONIUM IONS LEFT ON COLUMNS OF AMP–ASBESTOS AFTER BREAKTHROUGH EXPERIMENTS

| Concentration of influent solution (mg per 100 ml) | Remaining number of equivalents of $NH_4^+$ per mole of AMP |
|---|---|
| 496·5 Cs | 1·29, 1·18 |
| 311 Cs | 1·29 |
| 321 Rb | 0·57, 0·73 |
| 160·5 Rb | 1·14, 1·39, 1·32 |

## ION EXCHANGE CAPACITY OF AMP

AMP is known to have a cubic structure, being isomorphous with caesium molybdophosphate, whose crystal structure has been throughly studied.[4,5] The three ammonium ions of the AMP molecule could therefore be expected to be equivalent with respect to exchangeability. Hence, according to this reasoning, all the ammonium ions on AMP should be exchangeable for the relatively large alkali metal ions. Assuming the composition of AMP to be $(NH_4)_3PMo_{12}O_{40}\cdot 2H_2O$, its ion exchange capacity may then be calculated to be 1·57 m-eq/g.

An estimate of the practical ion exchange capacity of AMP for rubidium and caesium was obtained by analysing the columns of AMP–asbestos of the previous series of experiments for ammonia (after completion of the breakthrough experiments), using a micro-Kjeldahl method. Reproducibility of the results (Table 1) was only moderate. They show that a maximum of only about 60 per cent of the ammonium ions have been exchanged for caesium and about 80 per cent for rudibium. This is in agreement with observations by BUCHWALD and THISTLETHWAITE.[22] If treatment of the column with the caesium or rubidium solution had been prolonged, the conversion might have been more complete, but it is doubtful whether quantitative exchange of the ammonium ions for caesium or rubidium would have been obtained. A possible explanation for this might be that caesium (and to a lesser degree rubidium) ions gradually block up the channels in the AMP lattice, thereby inhibiting the mobility, and hence exchangeability, of the residual ammonium ions.

## CONCLUSION

In conclusion, a few other interesting observations on the exchange on AMP may be made here. As ammonium ions are the only exchangeable cations of AMP, this exchanger, like "strong-base" organic resins and unlike the zeolites, is monofunctional. Adherence to the mass action law could therefore have been expected.

[22] H. BUCHWALD and W. P. THISTLETHWAITE, *J. Inorg. Nucl. Chem.* **5**, 341 (1958).

For theoretical studies on ion exchange, synthetic organic resins are very well suited, but they tend to shrink and expand when the experimental conditions are varied, which is a greatly complicating factor. AMP, like inorganic zeolites, shows only negligible shrinking. However, the use of the latter for theoretical studies of ion exchange is limited by their polyfunctionality. AMP, it appears therefore, combines the advantages of both the "strong-base" organic resins and the zeolites.

As an ion exchanger, it is cheap, readily available and easily prepared in any laboratory. Ion exchange on AMP is completely reversible and adsorbed ions may be desorbed in the usual way by elution with suitable elutriants. AMP has the further advantage that it may be dissolved in a dilute alkaline solution and be reformed upon acidification.

In neutral or acidic solutions its solubility is sufficiently low to permit the use of columns of AMP for separating ions chromatographically. In pure water, however, it peptizes slowly. This difficulty is obviated by keeping it in contact with a dilute electrolyte solution, preferably one containing ammonium ions.

*Acknowledgement*—This paper is published by permission of the South African Council for Scientific and Industrial Research.

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 113 to 121. Pergamon Press Ltd. Printed in Great Britain.

# OBSERVATIONS ON REACTIONS OF URANIUM COMPOUNDS

H. J. BORCHARDT

General Engineering Laboratory, General Electric Company, Schenectady, New York

(*Received* 23 *February* 1959; *in revised form* 25 *March* 1959)

**Abstract**—The reaction of $U_3O_8$, uranium carbide, and uranium boride, each respectively, with the metals Fe, Ni, Cr and Nb were investigated with thermoanalytical techniques and X-ray analysis. The air oxidation of uranium carbide and boride as well as the interaction between $UO_2$, $U_3O_8$ and $Cr_2O_3$ was briefly examined. It was found that all the above metals reduce $U_3O_8$ rapidly well below 1000°C. No interaction between uranium carbide and said metals was observed. Only Ni was found to react with uranium boride with the formation of an unidentified phase. The mechanisms of $U_3O_8$ reduction and uranium carbide and boride oxidation are discussed in light of the data. New phases resulting from interaction of $Cr_2O_3$ with $U_3O_8$ and the oxidation of uranium boride are reported.

Vol. 12 9/60

THE solid state reactions of a number of uranium compounds have been investigated by means of differential thermal analysis, thermogravimetry and X-ray analysis. The reactions studied are as follows:

1. $U_3O_8$, uranium carbide, and uranium boride, each with the metals Fe, Ni, Cr and Nb.
2. $U_3O_8$ and $UO_2$, each with $Cr_2O_3$.
3. The oxidation of uranium carbide and uranium boride.

The purpose of this work is to survey a relatively broad area of uranium chemistry with a lesser emphasis on depth. Wherever possible, however, some mechanistic rationalization of the data is presented.

## APPARATUS AND PROCEDURES

### A. *Differential thermal analysis*

The DTA apparatus utilized in this study is a commercially available unit manufactured by the Robert L. Stone Company, Austin, Texas, and is described in industrial literature supplied by the manufacturer. All the measurements described herein were performed under the following conditions:

(1) Rate of temperature rise: approximately 16°C/min.
(2) Temperature range: 25–1000°C.
(3) Sensitivity: it differed for different measurements but for all cases it falls in a range whereby a temperature difference of 1°C results in a pen displacement between 0·85 and 2·5 in. on a standard 12 in. strip chart.
(4) Sample weight: approximately 0·8 g of powdered sample.
(5) Packing density: the powders are tapped into the sample well with no external pressure applied.
(6) Reference material: calcined alumina.
(7) Diluent: the samples are not diluted.
(8) Atmosphere: a static argon atmosphere is used in each case.

B. *Thermogravimetric analysis*

A Chevenard thermobalance was used which measures weight continually as the temperature of a material is raised. In the present work, temperature was raised at a rate of 10°C/min and measurements were made to approximately 1000°C.

C. *X-ray analysis*

A G.E. Model XRD-3D X-ray diffractometer was used for obtaining powder patterns on the materials of interest. When "$UO_2$" is reported, only the presence of a fluorite phase is implied which may or may not be stoicheiometric. The same comment applied to the other materials. In each case, $CuK_\alpha$ radiation was used, filtered through Ni. The reported relative intensities are the ratio peak heights on the diffractometer trace.

TABLE 1

| Reaction | 1%/min reaction temp. (°C) |
|---|---|
| 1. $3U_3O_8 + 4Fe \longrightarrow 2Fe_2O_3(?) + 9UO_2$ | 500 |
| 2. $5U_3O_8 + 4Nb \longrightarrow 2Nb_2O_5 + 15UO_2$ | 491 |
| 3. $3U_3O_8 + 4Cr \longrightarrow 2Cr_2O_3 + 9UO_2$ | 800 |
| 4. $U_3O_8 + 2Ni \longrightarrow 2NiO + 3UO_2$ | 896 |

## MATERIALS

The materials used in this study are listed below with their source or mode of preparation, average particle size as determined on a Fisher sub-sieve sizer, and analysis.

*Niobium:* 9·5 $\mu$. Minimum Nb content is 99·3 per cent. Maximum concentrations of impurities in per cent are as follows: C, 0·05; N, 0·03; O, 0·15; Si, 0·05; Fe, 0·10; Ta, 0·20; Ti, 0·05. H, 200 ppm; Mo, 500 ppm; Zr, 500 ppm.

*Chromium:* Electrolytic. 4·4 $\mu$. Minimum Cr content is 99·8 per cent. Maximum concentrations of impurities in per cent are as follows: C, 0·04; S, 0·04; Si, 0·03; Fe, 0·03; Al, 0·005; Ni, 0·01; Mn, 0·01; Cu, 0·01; O, 0·65; N, 0·005.

*Iron:* Electrolytic. 5·6 $\mu$. Minimum Fe content is 98·3 per cent. Maximum concentrations of impurities in per cent are as follows: C, 0·04; S, 0·03; Si, 0·02; Ni, 0·15; N, 0·008; O, 1·25.

*Nickel:* Carbonyl process. 3·6 $\mu$. Minimum Ni content is 99·85 per cent. Maximum concentrations of impurities in per cent are as follows: C, 0·09; S, 0·005; Co, 0·01; Mn, 0·01; Fe, 0·01.

$U_3O_8$: Oxidation of AEC high purity $UO_2$. 7·8 $\mu$. No further analysis.

$UB_2$: From Cooper Metallurgical Associates. 2 $\mu$. Uranium by direct analysis, boron by difference yields stoicheiometric formula, $UB_{2\cdot7}$.

$UC_2$: From AEC. Weight as $U_3O_8$ yields stoicheiometric formula $UC_{1\cdot69}$. No X-ray lines attributable to uranium oxide are present.

## RESULTS AND DISCUSSION

A. $U_3O_8$ + *metals*

DTA patterns of 50-50 w/o mixtures of the metals Fe, Ni, Cr and Nb, each with $U_3O_8$, (stoicheiometrically, a large excess of metal), are shown in Fig. 1. In the case of $U_3O_8$ + Fe, an exotherm indicative of reactions initiates at approximately 500°C and extends to 600°C. The small endotherms at 770°C and 920°C can be associated, respectively, with the Curie point of iron (unreacted excess) and the transition to $\gamma$-iron. After the measurement, the sample was cooled to room temperature in argon and subsequent X-ray analysis indicated that $U_3O_8$ has been completely reduced to $UO_2$. The same procedures were followed with $U_3O_8$ + Cr and $U_3O_8$ + Nb with the same results. In the case of $U_3O_8$ + Ni, a small quantity of $U_3O_8$ was still present after the DTA measurement.

Vol. 12 1959/6

The above results are summarized in Table 2. That the reactions listed in Table 2 can occur as written is known, of course, from thermodynamic considerations. The value of the described measurement lies in the fact that some indication is obtained of the temperature range in which the reaction rate becomes "appreciable". It is shown elsewhere[1] that the term "appreciable" can be defined quantitatively. Specifically, the temperature at which the initial reaction rate has a value of 1 per

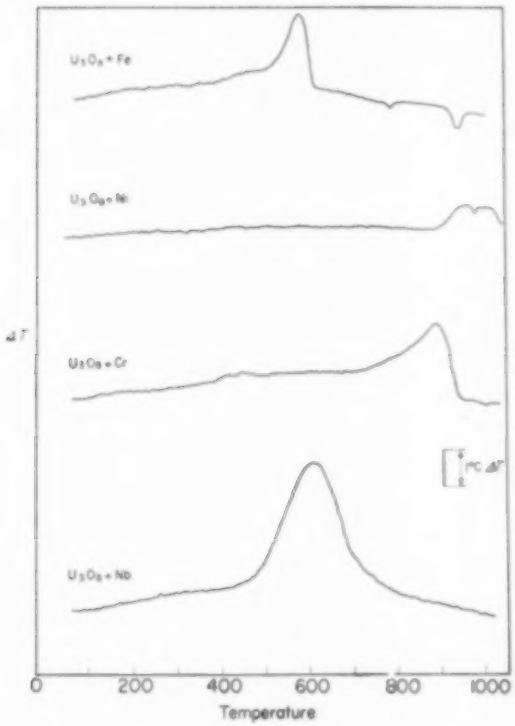



FIG. 1.—DTA patterns of $U_3O_8$ + metal mixtures.

cent conversion per minute, *under the particular set of experimental conditions employed*, can be calculated from the DTA trace. It is also shown[1] that 1 per cent per minute for powers in the 1–10 $\mu$ range corresponds approximately to a reaction rate of $10^{-6}$ cm/min in terms of rate of increase of product layer thickness. The temperatures to which the above considerations apply are given in Table 1.

Two general types of mechanisms can be postulated for reduction of $U_3O_8$ by metals. One involves mass transport by solid state diffusion processes only. In the other, $U_3O_8$ dissociates followed by reaction between $O_2$(g) and the metal as follows:

1. $$U_3O_8(s) \longrightarrow 3UO_2(s) + O_2(g)$$

2. $$O_2(g) + \text{metal}(s) \longrightarrow \text{metal oxide}(s)$$

[1] H. J. BORCHARDT, *J. Inorg. Nucl. Chem.* In press.

It has been shown[2] that the DTA data may be utilized to determine whether or not the mechanism involving the dissociation step is possible. These considerations reduce to the following:

The rate of the over-all reaction cannot exceed the rate of dissociation of $U_3O_8$ if the above equations correctly describe the mechanism. The *maximum* rate of dissociation can be calculated from the surface area and dissociation pressure. Alternately, the same calculation can yield the *lowest* temperature at which a particular rate of dissociation can occur. For the 7·8 $\mu$ particle size $U_3O_8$, this minimum temperature is 613°C, for a rate of 1 per cent conversion per minute. Thus, below 613°C, the dissociation pressure of $U_3O_8$ is too low to allow step (1) above to occur at an initial rate of 1 per cent per minute. In light of the data in Table 2, it follows that the reactions involving Fe and Nb are *not* proceeding by the dissociation mechanism cited above and the alternative solid state diffusion mechanism appears more likely in these cases.

B. $U_3O_8$, $UO_2 + Cr_2O_3$

Mixtures of $U_3O_8$ and $UO_2$, each with $Cr_2O_3$, were heated for 2 hr at 1000°C in argon on the thermobalance. No detectable weight change was observed in either case. X-ray analysis of the residues indicated that no reaction occurred in the case of $UO_2 + Cr_2O_3$. However, $U_3O_8$ did react with $Cr_2O_3$ to give rise to a new phase with X-ray lines given in Table 2.

Vol. 12 1959/6

TABLE 2

| Line | *d* | *I/Io* |
|---|---|---|
| 1 | 3·78 | 70 |
| 2 | 3·36 | 100 |
| 3 | 3·03 | 100 |
| 4 | 2·85 | 10 |
| 5 | 2·53 | 70 |
| 6 | 2·41 | 10 |
| 7 | 1·62 | 10 |

Studies with samples in the composition range, three moles $Cr_2O_3$ to two $U_3O_8$ indicate that the new phase contains U and Cr in the ratio of approximately 1 : 1 gramme atoms ($UCrO_x$) and that this phase has a very narrow solid solubility range.

C. *Uranium carbide, uranium boride + metals*

DTA patterns of 50-50 w/o mixtures of uranium carbide (69% $UC_2$, 31% UC) with the metals Fe, Ni, Cr and Nb show no behaviour that can be attributed to interaction. The observations with uranium boride were similar except for the case of uranium boride + Ni. Here a new phase appeared with X-ray lines as given in Table 3.

[2] H. J. BORCHARDT, *J. Amer. Chem. Soc.* **81**, 1529 (1959).

TABLE 3

| Line | *d* | *I/Io* | Line | *d* | *I/Io* | Line | *d* | *I/Io* |
|---|---|---|---|---|---|---|---|---|
| 1 | 4·55 | 15 | 8 | 2·61 | 20 | 15 | 2·08 | 30 |
| 2 | 3·91 | 15 | 9 | 2·58 | 35 | 16 | 1·98 | 100 |
| 3 | 3·77 | 15 | 10 | 2·50 | 50 | 17 | 1·89 | 10 |
| 4 | 3·52 | 10 | 11 | 2·36 | 75 | 18 | 1·76 | 30 |
| 5 | 3·35 | 15 | 12 | 2·25 | 85 | 19 | 1·71 | 15 |
| 6 | 2·82 | 25 | 13 | 2·17 | 10 | 20 | 1·68 | 10 |
| 7 | 2·66 | 20 | 14 | 2·13 | 20 | 21 | 1·62 | 20 |

D. *Oxidation of uranium carbide*

A sample of uranium carbide weighing 0·5938 g was heated in static air to 1000°C at a rate of temperature rise of 10°C/min on the Chevenard thermobalance. The rather unusual weight–temperature trace shown in Fig. 2 was obtained. From the weight changes at the various arrest points on the curve, an explanation can be obtained as follows:

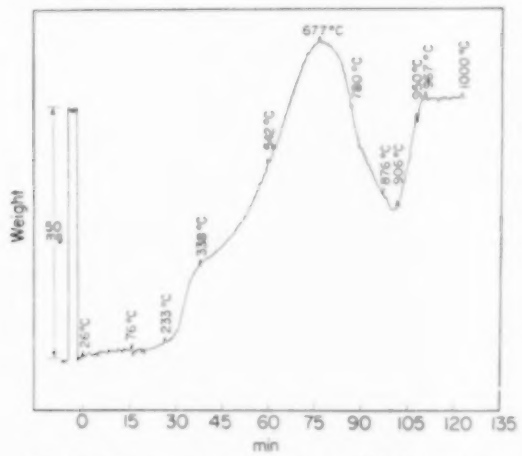



FIG. 2.—Thermogram of uranium carbide in static air.

1. *Composition of uranium carbide.* Assuming that the final product is $U_3O_8$, a weight gain of 0·043 g should be observed if the reactant is $UC_2$. The actual weight at 1000°C shows that a gain of 0·051 g takes place. The reactant, therefore, has an average composition of $UC_{1·69}$ or a mixture containing 31 per cent UC and 69 per cent $UC_2$.

2. *Composition at* 677°C. Since the weight at this temperature is greater than the final weight, it follows that some of the carbon must still be present. If the sample at 677°C consisted of $UO_2$ plus all the original carbon, weight gain of 0·074 g is expected. The observed weight gain is 0·062 g. It therefore appears that approximately $\frac{1}{4}$ of the carbon originally present is lost by 677°C.

3. *Composition at approximately* 900°C. If the weight loss between 677°C and the minimum in the curve at approximately 900°C was due to loss of all the *remaining* carbon, the weight loss should be 0·035 g. The observed weight loss of 0·034 g agrees well with this figure. If the mechanism postulated thus far is correct, the process between 900°C and 967°C is the oxidation of $UO_2$ to $U_3O_8$. The theoretical weight gain for this process is 0·023 g. A weight gain of 0·023 g is observed.

TABLE 4

| | Theoretical weight change (g) | Observed weight change (g) |
|---|---|---|
| 1. 150–680°C $UC_x + (1 + \frac{1}{4}x)O_2 \longrightarrow UO_2 + \frac{3}{4}xC + \frac{1}{4}xCO$ | + 0·062 | + 0·062 |
| 2. 680–900°C $2C + O_2 \longrightarrow 2CO$ | − 0·035 | − 0·034 |
| 3. 900–970°C $3UO_2 + O_2 \longrightarrow U_3O_8$ | + 0·023 | + 0·023 |

Table 4 summarizes the steps by which the observed weight–temperature behaviour can be consistently explained. Under the described experimental conditions step (2) begins to proceed as soon as carbon is formed, although at a slower rate than step (1), leading to a build-up of carbon. Step (3) does not occur until reaction (2) is complete; that is, $UO_2$ does not oxidize to $U_3O_8$ in the presence of carbon.

Vol. 12 1959/6

E. *Oxidation of uranium boride.*

A cursory study of the oxidation of uranium boride in air reveals that the process is a highly complex one. Under certain conditions, a new phase appears which presumably contains uranium, boron and oxygen. The colour of this material is green-yellow. The first sixteen X-ray lines of this phase are given in Table 5.

TABLE 5

| Line | *d* | *I/Io* | Line | *d* | *I/Io* |
|---|---|---|---|---|---|
| 1 | 5·30 | 57 | 9 | 2·63 | 24 |
| 2 | 4·92 | 49 | 10 | 2·59 | 59 |
| 3 | 4·44 | 100 | 11 | 2·46 | 14 |
| 4 | 3·88 | 100 | 12 | 2·33 | 24 |
| 5 | 3·34 | 54 | 13 | 2·21 | 32 |
| 6 | 3·12 | 49 | 14 | 2·61 | 22 |
| 7 | 2·94 | 92 | 15 | 2·11 | 62 |
| 8 | 2·75 | 14 | 16 | 2·06 | 57 |

A weight–temperature plot of uranium boride heated in air with temperature rising at a rate of 10°C/min, is shown in Fig. 3. A distinct break in the curve occurs

in the neighbourhood of 500°C. The residue resulting from this measurement contains the new phase. However, when uranium boride is placed directly into a furnace at 1000°C, this phase does not appear but, instead, the product is a black hard mass. X-ray diffraction shows $U_3O_8$ and $UO_2$ to be present. The presence of $B_2O_3$ is inferred from the stoicheiometry and the physical state of the residue (i.e. the uranium oxide is cemented into a hard mass by what is probably $B_2O_3$ glass).

In order to gain a little more insight into the nature of the oxidation process, isothermal measurements were performed between 400 and 1200°C, in air. Different processes appear to occur in different temperature ranges as follows:

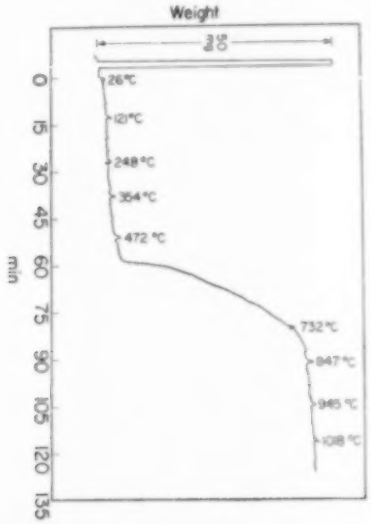



FIG. 3.—Thermogram or uranium boride in static air.

1. *Below* 500°C. A very slight weight gain occurs with no changes perceptible visually or by X-ray analysis on a time scale of hours.

2. 600–700°C. In 4 hr at 600°C, uranium boride is converted into a dark olive-green product. The X-ray pattern of this product indicates the presence of two very poorly crystalline phases: $U_3O_8$ and the new phase. No other phases can be discerned, specifically, no crystalline $UB_4$ is present.

Further reaction is very slow. The product above was heated to a total of 20 hr at 600°C, then 45 hr at 700°C and 23 hr at 800°C. The successive treatments resulted in an increase in the relative amount of the new phase with a corresponding decrease in $U_3O_8$ content. Both phases remain poorly crystalline, however. During these processes, the colour of the sample gradually becomes lighter.

The above sample was subsequently heated for 1 hr at 1000°C. This results in the formation of the unknown phase in a moderately well crystallized state, almost complete disappearance of $U_3O_8$ and a colour change of the sample to green-yellow. Fig. 4 shows the change in the first lines of the X-ray diffractometer trace as a result of the above operations.

3. *Above* 800°C. When uranium is inserted into a furnace at 800°C or above, a black, hard mass is formed very rapidly which by X-ray analysis is seen to contain $U_3O_8$ and $UO_2$. As previously mentioned, the presence of $B_2O_3$ is inferred from the stoicheiometry and physical state of the sample.

The new phase is thermally unstable above 900°C. Decomposition leads to the formation of $U_3O_8$ and probably $B_2O_3$. This decomposition occurs both in air and in

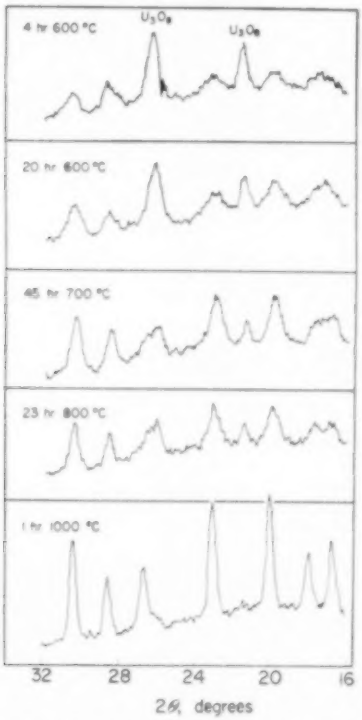



FIG. 4.—First few lines of the diffractometer trace of oxidized uranium boride. Note the diminution in the intensity of the $U_3O_8$ lines on the successive patterns.

argon. At 900°C, the first visual indication of decomposition is obtained after 4 hr. At 1150°C, decomposition is perceptible after 4 min. Heating for 23 hr at 800°C results in no detectable change. This, of course, does not imply that the phase is thermodynamically stable at or below 800°C.

It is interesting to note that the unknown phase forms most readily in a crystalline state at a temperature (1000°C) where it is unstable.

Although no pretences are made that the oxidation of uranium boride in air is understood, light is shed on certain coarse features of the process by the present data. These are as follows:

(1) Below 500°C the oxidation of uranium boride proceeds at an extremely slow rate.
(2) At approximately 500°C a change occurs, which leads to virtually catastrophic oxidation above this temperature.

Vol 12 1959/

(3) Between 500°C and 800°C two successive reactions are evident. First, a rapid reaction occurs leading to the formation of $U_3O_8$ and a new phase. This is followed by a much slower process whereby $U_3O_8$ gradually disappears.
(4) At or above 800°C, oxidation leads to a different set of products. The new phase does not appear and instead $U_3O_8$, $UO_2$ and $B_2O_3$ are formed. Note that the unidentified phase is quite stable at 800°C once it is formed.

## SUMMARY

(1) Under the described experimental conditions, the metals Fe, Ni, Cr and Nb reduce $U_3O_8$ to $UO_2$ rapidly well below 1000°C.
(2) No reaction was observed to occur between uranium carbide and the above metals.
(3) Only Ni was found to react with uranium boride with the formation of an unidentified phase.
(4) $Cr_2O_3$ reacts with $U_3O_8$ to form a new phase. Under the same conditions, $Cr_2O_3$ does not react with $UO_2$.
(5) The air oxidation of uranium carbide yields, initially, $UO_2$ and carbon. Thereafter, uranium carbide and free carbon compete for the available oxygen, the oxidation of uranium carbide occurring at the more rapid rate. $U_3O_8$ is not formed until all the free carbon has been oxidized.
(6) The air oxidation of uranium boride is very slow below 500°C, but proceeds catastrophically above this temperature. Between 500°C and 800°C, oxidation leads to the formation of a new phase. Above 800°C, oxidation leads to the formation of $U_3O_8$, $UO_2$ and $B_2O_3$.

Vol.
12
59/60

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 122 to 128. Pergamon Press Ltd. Printed in Great Britain.

# SOME METAL COMPLEXES OF CITRIC AND TRICARBALLYLIC ACIDS*

N. C. LI, A. LINDENBAUM and J. M. WHITE
Argonne National Laboratory and Duquesne University
Lemont, Illinois

(*Received* 6 *March* 1959)

**Abstract**—The formation constants of several metal complexes of citrate and tricarballylate, and of the "hydrogen complexes", i.e. complexes in which $HA^{2-}$ act as ligands, have been determined by a titrimetric method. For Mn(II), Cd(II), Zn(II) and Ni(II) complexes of citrate, the value of $K_{MA}/K_{MHA}$ varies from $10^{1.6}$ to $10^{1.9}$, the ratio increasing with increasing value of $K_{MA}$. The citrate complexes are more stable than the corresponding tricarballylate complex, as expected. The Co(II) and Mg complexes of citrate have reduction potentials which are too negative for direct polarographic method. In the pH region 1·9 to 2·5 the 1 : 1 uranyl-citrate complex has been shown to be a monomer with log $K_{MA} = 8{\cdot}5$.

As part of a continuing investigation of metal complexes of organic acids,[1] we report here the formation constants of several metal complexes of citrate and tricarballylate ($A^{3-}$). By the use of the titrimetric method of SCHWARZENBACH[2] (using metal ion concentration tenfold in excess over the ligand concentration), the formation constants of the "hydrogen complexes", i.e. complexes in which $HA^{2-}$ act as ligands, are also obtained.

MEITES[3a] studied the cadmium complex of citrate by means of a conventional polarographic method,[3b] while an e.m.f. method used by TREUMANN and FERRIS[3c] has yielded an extrapolated value of 5·37 for log $K_{Cd\ Cit^-}$. The Co(II) and Mg(II) complexes of citrate, however, have reduction potentials which are too negative and the reduction waves are irreversible. For the measurement of these metal complexes, an indirect polarographic method was developed.

FELDMAN and co-workers[4] have studied the uranyl-citrate system and have found that when equimolar mixtures of uranyl nitrate and citric acid are raised to pH 3·5, there is present a 1 : 1 uranyl-citrate complex as a dimer $(UO_2Cit^-)_2$. They also

* Work done in part at Argonne National Laboratory under the auspices of the U.S. Atomic Energy Commission. The work of N. C. LI and J. M. WHITE was supported in part by the U.S. Atomic Energy Commission through Contract No. AT (39-1)-1922 with Duquesne University. Presented at the International Conference on Co-ordination Chemistry at London, England, April 11–16, 1959.

(1a) N. C. LI, W. M. WESTFALL, A. LINDENBAUM, J. M. WHITE and J. SCHUBERT, *J. Amer. Chem Soc.* **79**, 5864 (1957); (b) J. SCHUBERT, E. LIND, W. M. WESTFALL, R. PFLEGER and N. C. LI, *Ibid.* **80**, 4799 (1958).

(2) G. SCHWARZENBACH, *Helv. Chim. Acta*, **33**, 947 (1950); H. SENN, *Der Einfluss von Substituenten auf die Stabilität von Chelatkomplexen*. Brunner Bodner, Zürich (1956).

(3a) L. MEITES, *J. Amer. Chem. Soc.* **73**, 3727 (1951); (b) I. M. KOLTHOFF and J. J. LINGANE, *Polarography*. Interscience, New York (1952); (c) W. B. TREUMANN and L. M. FERRIS, *J. Amer. Chem. Soc.* **80**, 5050 (1958); (d) N. C. LI, J. M. WHITE and R. L. YOEST, *Ibid.* **78**, 5218 (1956).

(4a) I. FELDMAN and W. F. NEUMAN, *J. Amer, Chem. Soc.* 2312 (1951); (b) W. F. NEUMAN, J. R. HAVILL and I. FELDMAN, *Ibid.* **73**, 3593 (1951); (c) I. FELDMAN, J. R. HAVILL and W. F. NEUMAN, *Ibid.* **76**. 4726 (1954).



Vol. 12 1959/6

studied the uranyl-citrate system over a wide range of pH; however, no quantitative value of the formation constant of any of the complexes is given. HEITNER and BOBTELSKY[5] state at pH $< 7$ the uranyl-citrate complex is the monomer, $UO_2Cit^-$, and gave the constant: $\log K_{MA} = 3{\cdot}16$. This value seems too low, in view of the formation constant reported for uranyl-oxalate:[6] $\log K_{MA} = 5{\cdot}82$. We have therefore redetermined the formation constant of the uranyl-citrate complex in the pH region where it is a monomer, and the result is reported here.

## EXPERIMENTAL

*Materials.* All chemicals used were C.P. grade. The 0·1 M stock solution of uranyl nitrate contained an equimolar amount of HCl, and was standardized by the gravimetric determination of uranium after ignition to $U_3O_8$. The solutions of citric acid and tricarballylic acid were checked by titration with standardized sodium hydroxide, and only fresh solutions were used.

*Procedure.* pH determinations were made with a Beckman Model G pH meter and a Radiometer, type PHM 3k, using a glass electrode with a saturated calomel electrode as the reference electrode. The instruments were standardized against standard buffer solutions at pH 4 and 7. Below pH 2·2 the instruments were calibrated with HCl–KCl solutions. During all titrations a stream of presaturated, nitrogen gas was passed through the titration vessel.

Polarographic measurements were made with a Sargent Model XXI or a Fisher Electropode polarograph in the manner previously described.[3,4]

## METHOD OF CALCULATION

(A) *Dissociation constants of* $H_3A$. The dissociation constants of the tricarboxylic acids, $H_3A$, which are necessary for calculating the formation constants of metal complexes with citrate or tricarballylate, are determined by the following equilibria present in aqueous solutions:

$$H_3A = H_2A^- + H^+; \qquad K_1 = (H_2A^-)(H^+)/(H_3A) \tag{1a}$$

$$H_2A^- = HA^{2-} + H^+; \qquad K_2 = (HA^{2-})(H^+)/(H_2A^-) \tag{1b}$$

$$HA^{2-} = A^{3-} + H^+; \qquad K_3 = (A^{3-})(H^+)/(HA^{2-}) \tag{1c}$$

Although citric acid has an OH group and acts as a tetrabasic acid, $H_4A$, toward Cu(II) and Fe(III),[7] we have found that for the metals reported in this paper, in the pH region below 9, citric acid acts as $H_3A$. (See Fig. 1 for titration curves of Ni(II) and uranyl-citric acid mixtures.)

Equations relating concentration of the tricarboxylic acid, concentration of NaOH and pH to the dissociation constants can be derived in a manner similar to those for glutathione and oxidized glutathione reported by LI *et al.*[8] The equations are

$$pK_1 = pH + \log\frac{g-2}{3-g} + \log\left[1 + \frac{K_2(g-1)}{(H^+)(g-2)}\right] \tag{2a}$$

$$pK_2 = pH + \log\frac{g-1}{2-g} - \log\left[1 + \frac{(H^+)(3-g)}{K_1\,(2-g)}\right] \tag{2b}$$

$$pK_3 = pH + \log\frac{g}{1-g} - \log\left[1 + \frac{(H^+)(2-g)}{K_2\,(1-g)}\right] \tag{2c}$$

(5) C. HEITNER and M. BOBTELSKY, *Bull. Soc. Chim. Fr.* 356 (1954).
(6) L. J. HEIDT, *J. Phys. Chem.* **46**, 624 (1942).
(7) R. C. WARNER and I. WEBER, *J. Amer. Chem. Soc.* **75**, 5086 (1953).
(8) N. C. LI, O. GAWRON and G. BASCUAS, *J. Amer. Chem. Soc.* **76**, 225 (1954).

where $g = [3T - (\text{NaOH}) - (\text{H}^+) + (\text{OH}^-)]/T$ and $T$ = total molar concentration of citric acid in solution.

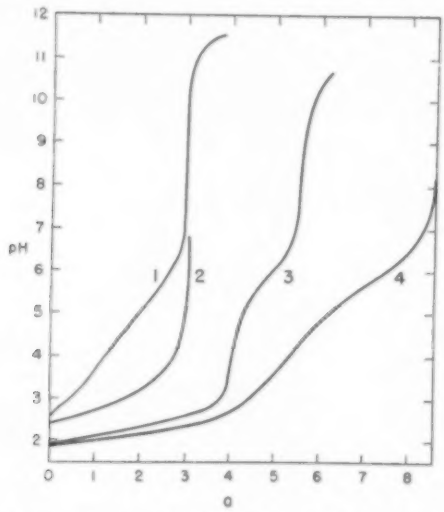



FIG. 1.—pH titration of: curve 1, 0·01 M citric acid, 0·15 M NaCl; curve 2, 0·005 M citric acid, 0·05 M $Ni(NO_3)_2$; curve 3, 0·01 M citric acid, 0·01 M $UO_2(NO_3)_2$, 0·01 M HCl, 0·11 M NaCl; curve 4, 0·02 M citric acid, 0·01 M $UO_2(NO_3)_2$, 0·01 M HCl, 0·11 M NaCl.
$a$ = moles NaOH per mole citric acid plus HCl, when present.

(B) *Formation constants of metal complexes and "hydrogen complexes" (after* SCHWARZENBACH[2]). The chelating agents are taken to be the ions $A^{3-}$ and $HA^{2-}$ and the formation constants are defined by the equations

$$M^{2+} + A^{3-} = MA^-; \qquad K_{MA} = (MA^-)/(M^{2+})(A^{3-}) \tag{3a}$$

$$M^{2+} + HA^{2-} = MHA; \qquad K_{MHA} = (MHA)/(M^{2+})(HA^{2-}) \tag{3b}$$

In the presence of tenfold excess metal ion over total acid concentration $T$, and in the pH region where $(A^{3-})$ may be neglected, we have the following equations:

$$T = (HA^{2-}) + (H_2A^-) + (H_3A) + (MHA) + (MA^-) \tag{4}$$

$$S = (HA^{2-}) + 2(H_2A^-) + 3(H_3A) + (MHA) \tag{5a}$$

$$= 3T - (\text{NaOH}) - (\text{H}^+) + (\text{OH}^-) \tag{5b}$$

$$g = S/T \tag{6}$$

$S$ may be defined as the total concentration of protons bound by $A$. Combination of equations (4), (5a) and (6) gives

$$g(MA^-) + (g-1)(MHA + HA^{2-}) + (g-2)(H_2A^-) + (g-3)(H_3A) = 0 \tag{7}$$

Since the metal ion is in tenfold excess, we may assume a constant concentration of free metal ion [(M) constant] and introduce the following quotients, as developed by SCHWARZENBACH[2]

Vol. 12 1959/6

$$K_{1'} = (\mathrm{MHA} + \mathrm{HA}^{2-})/(\mathrm{MA}^{-})(\mathrm{H}^{+}) \tag{8a}$$

$$K_{2'} = (\mathrm{H_2A}^{-})/(\mathrm{H}^{+})(\mathrm{MHA} + \mathrm{HA}^{2-}) \tag{8b}$$

By combining equations (3a), (3b) and (1), it can be shown readily that $K_{1'}$ and $K_{2'}$ are really groups of constants:

$$K_{1'} = [1 + K_{\mathrm{MHA}}(\mathrm{M})]/K_3K_{\mathrm{MA}}(\mathrm{M}) \tag{8c}$$

$$K_{2'} = [K_2(1 + K_{\mathrm{MHA}}(\mathrm{M})]^{-1} \tag{8d}$$

Combination of equations (8a), (8b) with equations (1) and (7) gives

$$g(1/K_{1'}) + (g - 1)(\mathrm{H}^{+}) + (g - 2)(\mathrm{H}^{+})^2K_{2'} + (g - 3)(\mathrm{H}^{+})^3K_2/K_1 = 0 \tag{9}$$

In equation (9), the unknowns are $K_{1'}$ and $K_{2'}$ and may be evaluated by any suitable mathematical device. In the present investigation, we proceeded as follows: Let

$$X = (\mathrm{H}^{+})(1 - g)/g; \qquad Y = \frac{1 - g}{(\mathrm{H}^{+})\,[(g - 2) + (g - 3)(\mathrm{H}^{+})/K_1]} \tag{10}$$

For a given $g$ in the regions $g = 1{\cdot}5 \pm 0{\cdot}2$ and $g = 0{\cdot}5 \pm 0{\cdot}2$, the values of $X$ and $Y$ were calculated, giving one point each on the $X$ and $Y$ axes. A straight line is drawn through these two points. Straight lines are drawn in exactly the same way for the other values of $g$ in the above regions. The $X$ and $Y$ values that correspond to the point of intersection of these straight lines yield the values of $1/K_{1'}$ and $K_{2'}$, respectively.

From equations (8c) and (8d), it is easy to derive the following relationships for the calculation of the formation constants

$$K_{\mathrm{MA}} = [K_{1'}K_{2'}K_2K_3(\mathrm{M}^{2+})]^{-1} \tag{11a}$$

$$K_{\mathrm{MHA}} = [(K_{2'}K_2)^{-1} - 1]/(\mathrm{M}^{2+}) \tag{11b}$$

If the total concentration of the metal salt, $T_m$, is very much larger than the total concentration of the tricarboxylic acid, so that $T_m$ may be substituted for $(\mathrm{M}^{2+})$ in equations (11), then the values of $K_{\mathrm{MA}}$ and $K_{\mathrm{MHA}}$ are easily obtained once the values of $K_{1'}$ and $K_{2'}$ are known. The uncertainties involved in locating $K_{1'}$ and $K_{2'}$ graphically result in uncertainties in the values of the formation constants reported in this paper by about 0·15 log unit.

(C) *Formation constant of uranyl-citrate complex.* We have found that by titration in the pH region 1·9–2·5, a 1:1 uranyl-citrate complex is formed with $\mathrm{A}^{3-}$ as the ligand. The following equations are derived:

$$(\mathrm{A}^{3-}) = \frac{[3T - (\mathrm{NaOH}) - (\mathrm{H}^{+}) + (\mathrm{OH}^{-})]\;K_1K_2K_3}{K_1K_2(\mathrm{H}^{+}) + 2K_1(\mathrm{H}^{+})^2 + 3(\mathrm{H}^{+})^3} \tag{12a}$$

$$\bar{n} = \frac{T - (\mathrm{A}^{-3})[K_1K_2K_3 + K_1K_2(\mathrm{H}^{+}) + K_1(\mathrm{H}^{+})^2 + (\mathrm{H}^{+})^3]/K_1K_2K_3}{T_m} \tag{12b}$$

Inasmuch as the 1:1 uranyl-citrate complex has been postulated to be a dimer and a monomer by NEUMAN *et al.*,[4] and by HEITNER and BOBTELSKY,[5] respectively, we propose the following equations

$$T_m = (\mathrm{M}^{2+}) + (\mathrm{MA}^{-}) + 2(\mathrm{M_2A_2}^{2-}) \tag{13}$$

$$\bar{n} = \frac{(MA^-) + 2(M_2A_2^{2-})}{T_m} \tag{14}$$

$$K_{M_2A_2} = (M_2A_2^{2-})/(M^{2+})^2(A^{3-})^2 \tag{15}$$

Combination of equations (3a), (13), (14) and (15) gives

$$\frac{\bar{n}}{(1-\bar{n})(A)} = K_{MA} + K_{M_2A_2} \times 2(1-\bar{n})T_m(A) \tag{16}$$

Equation (16) shows that if MA and $M_2A_2$ complexes both exist in solution, a plot of $\bar{n}/(1-\bar{n})(A)$ vs. $2(1-\bar{n})T_m(A)$ should yield a straight line, the intercept of which is $K_{MA}$ and the slope is $K_{M_2A_2}$. If the intercept of the linear plot is zero, only the dimer exists and the slope gives the value of $K_{M_2A_2}$. On the other hand, if the value of $\bar{n}/(1-\bar{n})(A)$ is constant, independent of variations in the value of $2(1-\bar{n})T_m(A)$, then only the monomer exists and the value of $\bar{n}/(1-\bar{n})(A)$ is equal to $K_{MA}$.

(D) *Indirect polarographic method for* Co(II)- *and* Mg(II)-*citrate complexes.* In essence the half-wave potentials of solution (i) and solution (ii) are determined: Solution (i) consisting of $5{\cdot}00 \times 10^{-4}$ M $Cd(NO_3)_2$, 0·05 M sodium citrate; solution (ii) has the same composition as (i), except that it also contains 0·0495 M $M(NO_3)_2$ where M = Co(II) or Mg(II). The first polarographic waves in both solutions are due to the reduction of the cadmium ion, and therefore the dropping mercury electrode reactions in both are reversible. These half-wave potentials for solutions (i) and (ii) are related by the equation[3c]

$$(E_{\frac{1}{2}})_{(i)} - (E_{\frac{1}{2}})_{(ii)} = -0{\cdot}030 \log (A)_{(i)}/(A)_{(ii)} \tag{17}$$

where (A) is the concentration of free citrate, and $(A)_{(i)}$ may be taken to be 0·0495 M. The value of $(A)_{(ii)}$ is easily calculated from equation (17). The values of $K_{CdA}$ and $K_{CdHA}$ are taken from experiments described in Section (B), from which the concentrations of CdA and CdHA can be obtained. The total concentrations of citric acid and metal in solution are given by the equations

$$T = (A^{3-}) + (CdA^-) + (CdHA) + (MA^-) + (MHA) + (HA^{2-}) + (H_2A^-) + (H_3A) \tag{17a}$$

$$T_m = (M^{2+}) + (MA^-) + (MHA) \tag{17b}$$

TABLE 1.—pH RESULTS OF SOME METAL COMPLEXES (25°, $\mu = 0{\cdot}15$)

| Complex | Log $K_{MA}$ | Log $K_{MHA}$ | Log $\frac{K_{MA}}{K_{MHA}}$ | Log $K_{MA}$ (as reported in lit.) |
|---|---|---|---|---|
| Citrate* | | | | |
| Mn(II) | 3·67 | 2·08 | 1·59 | 3·54[1]; 3·72[9] |
| Cd(II) | 3·98 | 2·28 | 1·70 | 4·2[3a]; 5·36[3c]‡ |
| Zn(II) | 4·85 | 2·96 | 1·89 | 4·71[1b] |
| Ni(II) | 5·11 | 3·19 | 1·92 | |
| Tricarballylate† | | | | |
| Ni(II) | 2·70 | 1·56 | 1·14 | |
| Mg(II) | 2·00 | 0·91 | 1·09 | |

* Citric acid: $pK_1 = 2{\cdot}94$, $pK_2 = 4{\cdot}34$, $pK_3 = 5{\cdot}62$.
† Tricarballylic acid: $pK_1 = 3{\cdot}50$, $pK_2 = 4{\cdot}63$, $pK_3 = 5{\cdot}95$.
‡ Value obtained by extrapolation to infinite dilution.
[9] J. S. WIBERG, *Arch. Biochem. Biophys.* **73**, 337 (1958).

Vol. 12 1959/6

The ratio of $K_{MHA}/K_{MA}$ is taken to be equal to the ratio $K_{CdHA}/K_{CdA}$, so that the concentration ratio (MHA)/(MA) is easily obtained. Since the concentrations of $HA^{2-}$, $H_2A^-$ and $H_3A$ are known in terms of $(A^{3-})$, pH and dissociation constants of citric acid, the values of $(MA^-)$ and (MHA) in equation (17a) and $(M^{2+})$ in equation (17b), and hence $K_{MA}$ and $K_{MHA}$ can be calculated.

## RESULTS

The acid dissociation constants of citric and tricarballylic acids and the formation constants of the metal complexes, determined in the manner described in Section (B) together with the values available in the literature, are summarized in Table 1.

TABLE 2.—POLAROGRAPHIC RESULTS FOR Co(II)- AND Mg(II)-CITRATE COMPLEXES ($25°$, $(E_{\frac{1}{2}})_{(1)} = -0.658$)

In solution (ii):

| $M(NO_3)_2$ | $-E_{\frac{1}{2}}$ | pH | $(A^{-3}) \times 10^8$ | (MA) | (MHA) $\times 10^8$ | $\mu$ | log $K_{MA}$ | log $K_{MHA}$ |
|---|---|---|---|---|---|---|---|---|
| Co(II) | 0·600 | 5·57 | 0·58 | 0·0472 | 1·1 | 0·06 | 4·83 | 3·19 |
| Mg(II) | 0·627 | 6·86 | 4·63 | 0·0445 | 0·1 | 0·09 | 3·29 | 1·60 |

TABLE 3.—TITRATION OF URANYL NITRATE–CITRIC ACID MIXTURES ($25°$)

(a) 50 ml solution containing 0·0100 M $UO_2(NO_3)_2$; 0·0100 M HCl; 0·0100 M citric acid; 0·110 M NaCl; plus $v$ ml 0·2986 M NaOH

| $v$(ml) | pH | pA | $\bar{n}$ | $2T_m(1-\bar{n})/(A^{3-}) \times 10^{10}$ | $\log \frac{\bar{n}}{(1-\bar{n})} \frac{1}{(A^{3-})}$ |
|---|---|---|---|---|---|
| 0·00 | 1·86 | | | | |
| 1·00 | 1·98 | 9·11 | 0·197 | 0·12 | 8·50 |
| 2·00 | 2·10 | 8·84 | 0·313 | 0·19 | 8·50 |
| 3·00 | 2·21 | 8·64 | 0·456 | 0·24 | 8·57 |
| 4·00 | 2·33 | 8·45 | 0·606 | 0·26 | 8·63 |
| 4·50 | 2·40 | 8·35 | 0·622 | 0·31 | 8·56 |

(b) Same as above, except using 0·0200 M citric acid in the initial soln.

| | | | | | |
|---|---|---|---|---|---|
| 0·00 | 1·81 | | | | |
| 1·00 | 1·91 | 8·97 | 0·235 | 0·16 | 8·46 |
| 2·00 | 2·01 | 8·75 | 0·356 | 0·22 | 8·49 |
| 3·00 | 2·11 | 8·47 | 0·473 | 0·34 | 8·43 |
| 3·50 | 2·16 | 8·35 | 0·544 | 0·38 | 8·43 |
| 4·00 | 2·21 | 8·24 | 0·613 | 0·41 | 8·43 |
| 5·00 | 2·32 | 7·98 | 0·757 | 0·46 | 8·47 |
| 6·00 | 2·48 | 7·60 | 0·890 | 0·49 | 8·50 |

(c) 50 ml soln. containing 0·0400 M $UO_2(NO_3)_2$; 0·0400 M HCl; 0·0500 M citric acid; plus $v$ ml 1·2970 M NaOH

| | | | | | |
|---|---|---|---|---|---|
| 0·00 | 1·37 | | | | |
| 3·00 | 1·89 | 8·76 | 0·392 | 0·80 | 8·57 |
| 3·85 | 2·01 | 8·51 | 0·557 | 1·02 | 8·61 |
| 5·00 | 2·23 | 8·05 | 0·771 | 1·49 | 8·58 |
| 5·80 | 2·48 | 7·52 | 0·923 | 1·67 | 8·60 |

The results on the Co(II)- and Mg(II)-citrate complexes, using the indirect polarographic method described in Section (D), are summarized in Table 2. Table 3 lists the results obtained with the pH titration of uranyl-citric acid mixtures. The values of pA and $\bar{n}$ were calculated by means of equations (12a) and (12b), respectively.

## DISCUSSION

From the data in Table 1 it is interesting to note for the citrate complexes that the value of $K_{MA}/K_{MHA}$ varies from $10^{1.6}$ to $10^{1.9}$,and that the ratio increases as the MA complex becomes more stable. The higher stability of the citrate over the tricarballylate complexes is as expected, because of the presence of the OH group in citric acid.

The formation constants of the Co(II) and Mg(II) complexes of citrate, obtained by an indirect polarographic method and listed in Table 2, are in fair agreement with values reported in the literature:[1,10] $\log K_{Co(II)\text{-citrate}} = 4{\cdot}61$; $\log K_{Mg\text{-citrate}} = 3{\cdot}25$.

Since the Co(II) and Mg complexes cannot be studied by means of the direct conventional polarographic method the demonstration of the validity of an indirect polarographic method for the measurement of such complexes may be of considerable usefulness. None of the formation constants of the "hydrogen complexes" listed in Tables 1 and 2 has been reported in the literature.

Curves 3 and 4 of Fig. 1 give the titration of uranyl nitrate-citric acid systems for 1:1 and 1:2 mixtures, respectively. The first inflexion point in curve 3 is accounted for by assuming complete neutralization of the three carboxylic hydrogens in citric acid in the formation of $UO_2$ $Cit^-$ chelate and the hydrochloric acid present in the uranyl nitrate stock solution. Comparison of curve 4 with curve 3 and with curve 1, which is the titration curve of citric acid by itself in the absence of uranyl nitrate, shows that the data of curve 4 correspond to the titration of curve 3 plus onefold excess citric acid. This indicates strongly that the uranyl ion does not form a 1:2 complex with citrate.

From Table 3 it is seen that in the pH region 1·9–2·5, $\log \bar{n}/(1-\bar{n})(A^{3-})$ remains essentially constant in spite of a fourteenfold variation in the values of $2T_m(1-\bar{n})(A^{3-})$. Such constancy indicates, from equation (16), that only the monomer exists. The average value of $\log K_{MA}$ is calculated to be 8·5. The titration data above pH 2·5 were not used in the calculation because of the well-known tendency of uranyl to undergo hydrolysis at higher pH. HEITNER and BOBTELSKY[5] report for uranyl citrate: $\log K_{MA} = 3{\cdot}16$, whereas HEIDT[6] reports for uranyl-oxalate: $\log K_{MA} = 5{\cdot}82$. It would seem that our value of $\log K_{MA}$ for uranyl-citrate complex is more reasonable, inasmuch as the citrate anion is expected to exert a greater affinity for a divalent metal cation than the oxalate anion.

It must be mentioned that in our calculations we have used the assumption[8] that $(H^+)$ equals approximately to $10^{-pH}$. If for citric acid one uses an approximate activity coefficient of 0·8 for $H^+$ at $\mu = 0{\cdot}15$, so that $(H^+)$ equals approximately $10^{-pH/0{\cdot}8}$ and the dissociation constant equals approximately $10^{-pK/0{\cdot}81}$, the values of $\log \bar{n}/(1-\bar{n})(A^{3-})$ in Table 3 still remain essentially constant. The average value of $\log K_{MA}$ now becomes 8·6.

*Acknowledgement*—The authors are indebted to Professor G. SCHWARZENBACH of the Eidg. Technischen Hochschule, Zürich, Switzerland, for helpful discussions regarding uranyl-citrate complex.

[10] A. B. HASTINGS, F. C. MCLEAN, L. EICHELBERGER, J. L. HALL and E. DACOSTA, *J. Biol. Chem.* **107**, 351 (1934).

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 129 to 135. Pergamon Press Ltd. Printed in Great Britain.

# EXTRACTION FROM SOLUTIONS OF PERCHLORIC ACID BY TRIBUTYLPHOSPHATE—I

## PARTITION COEFFICIENTS FOR ZIRCONIUM, THORIUM, CERIUM, PROMETHIUM AND YTTRIUM

S. SIEKIERSKI

Radiochemical Laboratory, Institute of Nuclear Research, Warsaw

(*Received* 30 *April* 1959)

**Abstract**—Zirconium, thorium, cerium, promethium and yttrium are well extracted by TBP from concentrated solutions of perchloric acid. Partition coefficients increase steadily with increasing acid concentration, except at low acidities. Thorium is better extracted than zirconium and the ratio of partition coefficients is constant at all acidities. Cerium and promethium have the same partition coefficient, and the coefficient for yttrium is somewhat smaller.

Vol. 12 59/60

Two factors seem to be most important for the partition of inorganic salts between water and organic solvents. These are:

1. The difference in solvation free energies in water and the organic solvent for both cation and anion.

2. The complex-forming tendency of the anion. The difference between the solvation free energies of an ion in two solvents of different dielectric constant has been treated by BJERRUM.[1] The following conclusion, as applied to the extraction of ions may be drawn from his results: the extraction into the organic phase increases with decreasing charge and increasing radius of ion. Although this theory is somewhat oversimplified, nevertheless it should be qualitatively true, particularly for anions. Considering only solvation free energies we may conclude that perchlorates should be capable of being well extracted, since $ClO_4^-$ is a large ion with small charge. A second factor favouring the extraction of perchlorates from concentrated solutions of perchloric acid might be the high activity of the salts in such solutions. Owing to this high activity the overall free energy change for transfer of the salt from solution in perchloric acid to the organic phase may be highly negative, and as a consequence extraction may be good. On the other hand, the complex-forming tendency of perchlorates is very small and as the ability to form extractable complexes greatly favours the extraction, small partition coefficients would be expected. Summing up: the extraction of perchlorates should be rather small at low acidities but large at high acid concentrations. This conclusion seemed to be confirmed only by the work of MURBACH and MCVEY,[2] as in other works[3–6] on the extraction of perchlorates high

[1] N. BJERRUM and E. LARSSON, *Z. Phys. Chem.* A **127**, 358 (1927); N. BJERRUM and E. JOZEFOWICZ, *Z. Phys. Chem.* A **159**, 194 (1932).
[2] E. W. MURBACH and W. H. MCVEY, LRL Report-115 (1954).
[3] P. C. YATES, R. LARAN, R. E. WILLIAMS and T. E. MOORE, *J. Amer. Chem. Soc.* **75**, 2212 (1953).
[4] W. LIBUS, M. SIEKIERSKA and Z. LIBUS, *Roczniki Chem.* **31**, 1293 (1957).
[5] M. BRANICA and E. BONA, *Proceedings of Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, P/2412.
[6] W. B. SHEVTCHENKO, I. W. SHILIN and A. S. SOLOVKIN. *J. Inorg. Chem. U.S.S.R.* **3**, 225 (1958).

$HClO_4$ concentrations were not employed. To verify the conclusions concerning the extraction of perchlorates, and to gather more information about the dependence of extraction on the acid concentration, partition coefficients for Zr, Th, Pm, Y and $Ce^{III}$ have been determined in solutions of various $HClO_4$ concentrations. The organic solvent employed was tributylphosphate (TBP) and in the case of zirconium TBP and hexone.

## EXPERIMENTAL

*Reagents*

The following radioactive indicators were used: $^{95}Zr$, $^{144}Ce$, $^{91}Y$, $^{147}Pm$. $^{95}Zr$ was separated from its daughter $^{95}Nb$ by the method described by HUFFMAN and BEAUFAIT.[7]

The solutions of Zr, Ce and Y carriers were prepared by evaporating the nitrates with perchloric acid, and dissolving in the appropriate amount of $HClO_4$.

TBP was purified by the method described by ALCOCK *et al.*[8] Hexone was purified by distillation. $HClO_4$ used was AnalaR grade.

*Partition measurements*

Partition coefficients $k$ = conc.(org)/conc.(aq) were determined by shaking 15 ml of each phase together for approximately 20 min, centrifuging and separating the phases for analysis. The solutions were not thermostated, but the temperature was fairly constant at 21–25°C.

In all experiments with radioactive indicators inactive carriers were added to make the concentration 0·00068 M. For promethium cerium carrier was used. In the case of thorium the solution employed was 0·1025 M.

Activity measurements on both phases were carried out with a liquid counter. The results were corrected for liquid density. In the case of cerium, activity measurements were carried out after the equilibrium between $^{144}Ce$ and its daughter $^{144}Pr$ had been established.

Thorium was determined gravimetrically as $ThO_2$.

The concentration of perchloric acid in both phases was determined potentiometrically (in the TBP phase after addition of ethyl alcohol). In the case of thorium-containing samples, results were corrected for the number of $OH^-$ equivalents used up in thorium hydroxide precipitation. It was assumed, that four $OH^-$ ions are used up for each $Th^{+4}$ ion.

## RESULTS AND DISCUSSION

### *Effect of varying the* $HClO_4$ *concentration*

The partition coefficients for zirconium, thorium, cerium, promethium and yttrium are shown in Table 1 and plotted logarithmically in Fig. 1. (The data for cerium are not shown in Fig. 1 for the sake of clarity.) The concentration of $HClO_4$ indicated is that of the aqueous phase after equilibrium between two phases has been established.

The following conclusions may be drawn from the experimental results:

High partition coefficients for all tri- and tetravalent cations are obtained at high acidities. The largest experimentally determined partition coefficient is that for zirconium $k_{Zr} \cong 5000$ at 9·27 M $HClO_4$. But from the shape of the curves in Fig. 1 it may be inferred that much higher values, particularly for thorium, can be obtained. This result confirms the assumption made in the introduction as to the good partition of perchlorates from concentrated solutions of $HClO_4$.

The curves representing the dependence of log $k$ on $HClO_4$ concentration are very

[7] E. H. HUFFMAN and L. BEAUFAIT, *J. Amer. Chem. Soc.* **71**, 3179 (1949)
[8] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).

Vol. 12 1959/6

Vol. 12 59/60



TABLE 1.—VARIATION OF THE EXTRACTION COEFFICIENT $k$, WITH THE CONCENTRATION OF PERCHLORIC ACID IN THE AQUEOUS PHASE FOR Zr, Th, $Ce^{111}$, Pm AND Y. SOLVENT USED—TBP

| Zr | | Th | | $Ce^{111}$ | | Pm | | Y | |
|---|---|---|---|---|---|---|---|---|---|
| $HClO_4$ conc. (M) | $k$ | $HClO_4$ conc. (M) | $k$ | $HClO_4$ conc. (M) | $k$ | $HClO_4$ conc. (M) | $k$ | $HClO_4$ conc. (M) | $k$ |
| 3·42 | 0·0018 | 2·13 | 0·050 | 0·84 | 0·048 | 0·55 | 0·052 | 0·55 | 0·039 |
| 4·59 | 0·009 | 3·00 | 0·092 | 1·57 | 0·040 | 0·94 | 0·045 | 0·95 | 0·033 |
| 5·02 | 0·018 | 3·84 | 0·22 | 2·60 | 0·051 | 1·74 | 0·040 | 1·75 | 0·029 |
| 5·74 | 0·076 | 4·68 | 0·77 | 3·31 | 0·079 | 2·57 | 0·051 | 2·59 | 0·037 |
| 6·27 | 0·23 | 5·02 | 1·5 | 4·32 | 0·16 | 3·42 | 0·082 | 3·46 | 0·057 |
| 6·77 | 1·0 | 5·55 | 4·0 | 5·16 | 0·30 | 4·30 | 0·16 | 4·33 | 0·11 |
| 7·37 | 6·5 | 5·97 | 13 | 5·97 | 0·93 | 5·13 | 0·37 | 5·20 | 0·23 |
| 7·51 | 8·3 | 6·35 | 31 | 6·87 | 3·8 | 5·99 | 1·1 | 6·05 | 0·64 |
| 7·87 | 33 | 6·71 | 46 | 7·65 | 18 | 6·81 | 4·0 | 6·89 | 2·0 |
| 8·29 | 133 | 6·97 | 200 | 8·38 | 76 | 7·81 | 21 | 7·77 | 9·0 |
| 8·55 | 400 | | | 8·98 | 284 | 8·33 | 77 | 8·43 | 40 |
| 9·27 | 5000 | | | | | 8·96 | 280 | 9·02 | 130 |

steep. In the case of zirconium the partition coefficient increases $4 \times 10^4$ times, when the concentration of $HClO_4$ increases from 4·59 to 8·55 M The shapes of the curves at higher $HClO_4$ concentrations are similar for all tri- and tetravalent cations, but the slope is higher for tetravalent. This is in qualitative agreement with the fact, that the co-ordination number with respect to $ClO_4^-$ ions should be higher for tetravalent cations.

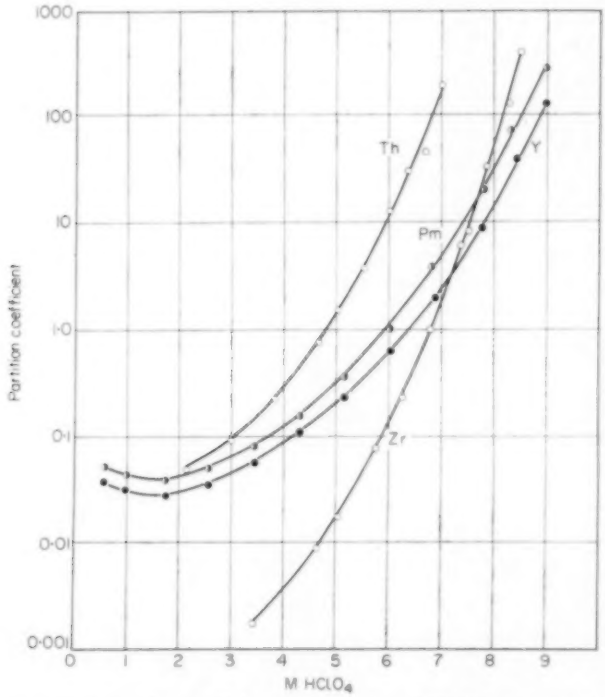



FIG. 1.—The partition coefficient as a function of $HClO_4$ concentration.

One of the most striking features of all curves is the absence of an inflexion, or a maximum in concentrated $HClO_4$ solutions, which are observed in the case of the extraction from nitric acid solutions. On the other hand a minimum is observed for rare earths and yttrium at low $HClO_4$ concentrations, the position of this minimum being independent of the nature of the extracted cation.

The semiquantitative discussion of the shape of the curves may be best carried out using an equation similar to that given by HESFORD and MCKAY[9] for the case of the extraction from nitric acid solutions: $k = K\, f_0\, (ClO_4^-)^p\, y_{\pm M}{}^{p+1} [TBP]^q / y_M$. In this equation $k$ is the partition coefficient, $K$ the equilibrium constant, $f_0$ that part of the total metal in the aqueous phase which is present in the form of simple cations, $y_{\pm M}$ and $y_M$ are mean molar activity coefficients of the salt in the aqueous and organic phases, terms in parenthesis denote concentrations and in square brackets denote activities, $p$ and $q$ denote the number of $ClO_4^-$ ions and TBP molecules attached to the metal in the organic phase.

[9] E. HESFORD and H. A. C. MCKAY, *Trans. Faraday Soc.* **54**, 573 (1958).

Vol. 12 1959/6

On the basis of this equation the absence of a maximum or an inflexion on the curve log $k$ vs. $HClO_4$ concentration indicates that the product $f_0\,(ClO_4^-)^p y_{\pm M}^{p+1}$ increases steadily with $HClO_4$ concentration. The last two terms in this product are known to increase with $HClO_4$ concentration because $HClO_4$ is highly dissociated in concentrated solutions, and $y_{\pm M}$ should behave similarly to $y_{\pm HClO_4}$. In view of the very steep slope of the log $k$ curve we may assume that $f_0$ does not diminish significantly. It would be in accord with known slight tendency of perchlorates to form complexes.

Very high partition coefficients at high $HClO_4$ concentrations indicate, that despite the fact that the ability to form extractable complexes greatly favours extraction, this factor can be made up for by others. The most important, as indicated in the introduction, is the activity term. The activity coefficient of a micro-amount of a salt in a concentrated solution of $HClO_4$ should depend on the concentration in the same way as the activity coefficient of the $HClO_4$. It is well known, that the activity coefficient of $HClO_4$ increases very rapidly with the concentration, and as in the above equation the activity coefficient appears as a high power the steep slope of the curve log $k$ vs. $HClO_4$ concentration may be qualitatively explained. To obtain a more quantitative agreement the expression of log $k_{Zr}$ − log $y_{\pm HClO_4}$ − 2 log (TBP) was plotted against the logarithm of the mean $HClO_4$ activity. No straight line was obtained, probably because the activities in the organic phase were neglected.

TABLE 2.—RATIO OF THE PARTITION COEFFICIENTS FOR Th AND Zr AS A FUNCTION OF PERCHLORIC ACID CONCENTRATION. SOLVENT USED—TBP

| $HClO_4$ conc. (M) | 4·00 | 4·50 | 5·00 | 5·50 | 6·00 | 6·50 | 7·00 |
|---|---|---|---|---|---|---|---|
| $\frac{k_{Th}}{k_{Zr}}$ | 67 | 65 | 72 | 73 | 68 | 72 | 71 |

As may be seen from Fig. 1 and Table 2 the partition coefficient for thorium is higher than for zirconium and the ratio $k_{Th}/k_{Zr} \sim 70$ is fairly constant at all acidities. This behaviour is quite different from that in nitric acid, where the extraction of zirconium is smaller than thorium at low acidities, but greater at higher acidities.[10] The constancy of this ratio indicates that $p$, $q$ and $y_{\pm M}$ are the same for thorium and zirconium, and that both ions exist in the same chemical form in the water phase at all acidities, probably as simple uncomplexed cations. The better extraction of thorium may be explained on the basis of the simple electrostatic theory. According to this theory the (positive) free energy change of transfer of a cation from water to a medium with lower dielectric constant decreases with increasing ionic radius, being thus lower for thorium than for zirconium.

The ratio $k_{Ce}/k_{Pm}$ is constant over the total range of acidities and is equal to one (as may be readily seen from Table 1). Such behaviour should be expected in the case of the extraction of cerium and promethium from $HClO_4$ solutions, as their crystal radii are very similar and they probably form only very weak complexes in the water phase with $ClO_4^-$ ions. All factors in the above equations are therefore identical for both cations.

The ratio $k_{Ce}/k_Y$ is greater than one and increases somewhat with the $HClO_4$

[10] D. F. PEPPARD, G. W. MASON and J. L. MAIER, *J. Inorg. Nucl. Chem.* 3, 215 (1956).

concentration although the shapes of the curves are similar and the difference in partition coefficients small. The better extraction of cerium by comparison with yttrium may be explained in the same manner as in the case of thorium and zirconium. In the extraction from nitric acid solutions the partition coefficients are higher for yttrium than for cerium[11] because the tendency to form extractable complexes increases with decreasing radius. As in the case of the perchlorates this tendency is small for both cations, other factors such as hydration energies and activity coefficients play a more important role, but these latter factors seem not to differ greatly.

It follows from the equation given by Hesford and McKay, that partition coefficients should tend towards zero as the concentration of acid decreases, if the activity coefficients in the organic phase do not change appreciably. In the case of the trivalent perchlorates investigated the partition coefficients increase somewhat when the concentration of $HClO_4$ decreases below about 1·7 M. The non-zero extraction at low $HClO_4$ concentrations deserves further investigations.

*Effect of varying the* TBP *concentration*

To determine $q$, the number of TBP molecules attached to the cation in the organic phase, the dependence of the partition coefficient for cerium on the TBP concentration, at constant composition of aqueous phase, has been investigated. Benzene was used as a diluent for TBP, since with kerosene a third, $HClO_4$-rich phase appeared. Results are shown in Fig. 2. At very low TBP concentrations an approximately

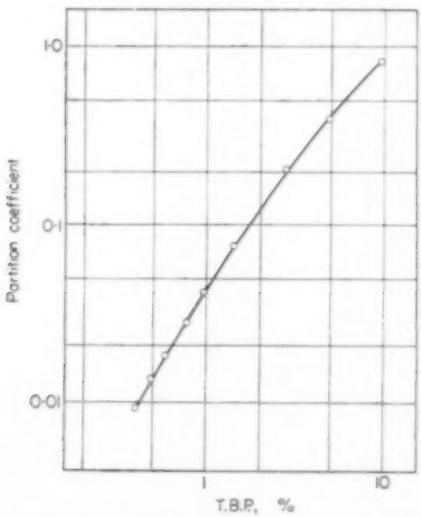



FIG. 2.—The partition coefficient of $Ce^{III}$ as a function of TBP concentration. Concentration of $HClO_4$ in aqueous phase 7·78 M.

straight line was obtained of slope 1·6. The slope of the curve decreases somewhat with increasing TBP concentration. This result shows clearly, that non-ideality is probably more marked in the system $HClO_4$–TBP-diluent, than in the system $HNO_3$–TBP-diluent.

[11] D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* 4, 304 (1957).

Vol. 12 1959/6

*The influence of* $NaClO_4$ *and tetrabutylammonium perchlorate*

The influence of both perchlorates has been investigated only for zirconium. Results for $NaClO_4$ are shown in Table 3. Partition coefficients for equimolar $HClO_4$

TABLE 3.—INFLUENCE OF ACIDITY ON THE EXTRACTION OF Zr. SOLVENT USED—TBP

| $HClO_4$ conc. (M) | $NaClO_4$ conc. (M) | $k_{Zr}$ | |
|---|---|---|---|
| | | for mixed solution | for equimolar $HClO_4$ conc. |
| 4·19 | 1 | 0·018 | 0·029 |
| 3·87 | 2 | 0·035 | 0·10 |
| 3·39 | 3 | 0·083 | 0·30 |

concentration have been determined by interpolation of the data in Table 1. It may be seen from Table 3 that $HClO_4$ is a better extracting agent for zirconium than $NaClO_4$, in the range of concentrations investigated. Perhaps the activity coefficient of zirconium perchlorate is smaller in a mixed solution $HClO_4$–$NaClO_4$ than in pure $HClO_4$.

The presence of 0·1 M tetrabutylammonium perchlorate in the TBP phase has no effect on the zirconium extraction from 4·58 M perchloric acid solution (equilibrium acid concentration). We could not also extract zirconium from 10·4 M $HClO_4$ solution by 0·1 M tetrabutylammonium perchlorate in chloroform. This indicates, that anionic complexes with $ClO_4^-$ ions can not be formed in the TBP and chloroform phases.

*The influence of temperature*

The influence of temperature on the partition coefficients for zirconium and cerium has been investigated in the temperature range 15–30°C. Somewhat unexpectedly a positive value for zirconium $\Delta k_{Zr}/\Delta t \cdot k_{Zr} = +0{\cdot}017$ at 7·42 M $HClO_4$, and a negative for cerium $\Delta k_{Ce}/\Delta t \cdot k_{Ce} = -0{\cdot}011$ at 5·95 M $HClO_4$, have been obtained.

*The extraction by hexone*

The partition results for zirconium are shown in Table 4. It may be seen, that the

TABLE 4.—EXTRACTION OF Zr FROM PERCHLORIC ACID SOLUTIONS BY HEXONE

| $HClO_4$ conc. (M) | 1·15 | 1·46 | 2·10 | 2·19 | 2·59 | 2·64 | 3·11 | 3·26 |
|---|---|---|---|---|---|---|---|---|
| $k_{Zr}$ | 0·00077 | 0·0018 | 0·0084 | 0·0096 | 0·022 | 0·034 | 0·048 | 0·073 |

extraction by hexone is better than by TBP in the range of acidities investigated. At perchloric acid concentration of about 4 M there is complete miscibility of the hexone and water phases.

Work on the extraction of tri- tetra- and hexa-valent plutonium from $HClO_4$ solutions by TBP is now in progress.

*Acknowledgement*—The author is indebted to J. SZYDLOWSKA for assistance in the determination of partition coefficients.

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 136 to 140. Pergamon Press Ltd. Printed in Great Britain.

# TRI-n-BUTYL PHOSPHATE AS AN EXTRACTING AGENT FOR INORGANIC NITRATES—VII

## THE TRIVALENT ACTINIDE NITRATES

G. F. BEST, E. HESFORD and H. A. C. MCKAY
Atomic Energy Research Establishment, Harwell, Didcot, Berks

(*Received* 30 *April* 1959)

**Abstract**—The trivalent actinide nitrates resemble the trivalent lanthanide nitrates in their extractability by tri-n-butyl phosphate (TBP). The resemblance is especially close for elements of the same ionic radius. In both series the element with a half-filled *f*-shell (Gd or Cm) is rather less extractable than might have been expected from the behaviour of its neighbours.

THE interesting results obtained in the extraction by tri-n-butyl phosphate (TBP) of the trivalent rare earth nitrates[1] suggest the desirability of studying the trivalent actinides. The range of actinides which can be studied is, however, unfortunately limited. Americium is the first whose trivalent state is fully stable in nitric acid solution though plutonium (III) can be studied up to about 2·5 M $HNO_3$, provided a trace of sulphamate is present to destroy nitrous acid. At the higher end, einsteinium was the heaviest actinide readily available to us.

Vol.
12
1959/6

### EXPERIMENTAL

The partition coefficients were determined at 25°C by the method [2] previously described. The isotopes used were $^{239}Pu$ (with small amounts of higher isotopes), $^{241}Am$, $^{244}Cm$, $^{249}Bk$, $^{252}Cf$ (containing 10% $^{250}Cf$ by counts) and $^{253}E$. $^{249}Bk$ was determined by means of a $\beta$-proportional counter, using very thin sources, and the other isotopes by standard $\alpha$-counting.

### RESULTS AND DISCUSSION

#### *Formulae of the* TBP-*solvates*

The formula $Am(NO_3)_3 \cdot 3TBP$ for the principal americium species in the TBP phase, has been established by experiments[3] in which the TBP concentration in an inert diluent (kerosene) was varied over the range 1·5–10% v/v. Since all the trivalent lanthanide nitrates yield tri-solvates with TBP, this result makes it highly probable hat all the trivalent actinide nitrates do the same.

(1) E. HESFORD, E. JACKSON and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **9**, 279 (1959).
(2) K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 100 (1957).
(3) T. V. HEALY and H. A. C. MCKAY, *Rec. Trav. Chim.* **75**, 730 (1956).

(100% TBP throughout)

| $HNO_3$ conc. (aq.) (M) | Partition coefficient (org./aq.) | $HNO_3$ conc. (aq.) (M) | Partition coefficient (org./aq.) | $HNO_3$ conc. (aq.) (M) | Partition coefficient (org./aq.) |
|---|---|---|---|---|---|
| Plutonium | | Americium | | Curium | |
| 0·18 | 0·0188 | 0·550 | 0·073 | 0·450 | 0·0486 |
| 0·30 | 0·0433 | 1·10 | 0·128 | 0·920 | 0·103 |
| 0·75 | 0·127 | 1·71 | 0·182 | 2·40 | 0·198 |
| 0·87 | 0·147 | 2·35 | 0·213 | 3·89 | 0·280 |
| 0·88 | 0·152 | 2·70 | 0·227 | 4·96 | 0·249 |
| 1·16 | 0·173 | 3·90 | 0·257 | 6·20 | 0·254 |
| 1·44 | 0·191 | 4·70 | 0·262 | 7·30 | 0·231 |
| 1·58 | 0·208 | 5·50 | 0·220 | 8·42 | 0·253 |
| 1·61 | 0·209 | 7·65 | 0·192 | 10·1 | 0·407 |
| 1·70 | 0·220 | 8·90 | 0·223 | 11·9 | 0·812 |
| 1·91 | 0·355 | 10·1 | 0·261 | 13·7 | 1·97 |
| 2·10 | 0·216 | 11·8 | 0·475 | 15·2 | 4·51 |
| 2·12 | 0·224 | 12·7 | 0·642 | | |
| 2·25 | 0·267 | 15·3 | 2·23 | | |
| 2·53 | 0·258 | | | | |
| 2·62 | 0·304 | | | | |
| 2·68 | 0·292 | | | | |
| 2·72 | 0·270 | | | | |
| Berkelium | | Californium | | Einsteinium | |
| 0·35 | 0·0526 | 0·410 | 0·0872 | 0·330 | 0·062 |
| 0·468 | 0·0755 | 0·890 | 0·187 | 0·480 | 0·101 |
| 0·914 | 0·165 | 1·94 | 0·329 | 0·830 | 0·186 |
| 2·04 | 0·317 | 2·93 | 0·392 | 1·40 | 0·275 |
| 2·81 | 0·343 | 4·17 | 0·488 | 1·72 | 0·323 |
| 3·94 | 0·410 | 4·79 | 0·510 | 2·57 | 0·414 |
| 4·60 | 0·449 | 5·82 | 0·489 | 3·80 | 0·498 |
| 5·18 | 0·449 | 6·47 | 0·520 | 5·16 | 0·508 |
| 6·25 | 0·465 | 6·90 | 0·544 | 6·22 | 0·508 |
| 6·29 | 0·473 | 8·07 | 0·595 | 7·22 | 0·534 |
| 6·97 | 0·485 | 8·20 | 0·84 | 7·87 | 0·611 |
| 7·67 | 0·507 | 9·56 | 0·950 | 9·09 | 0·835 |
| 7·71 | 0·517 | 11·1 | 1·51 | 10·8 | 1·53 |
| 8·85 | 0·562 | 12·5 | 3·07 | 11·0 | 1·60 |
| 10·1 | 0·729 | 13·1 | 5·80 | 12·1 | 2·90 |
| 10·5 | 0·962 | 13·8 | 6·20 | 12·9 | 4·23 |
| 11·9 | 1·89 | 15·5 | 15·1 | 13·6 | 6·06 |
| 12·7 | 2·38 | | | 13·8 | 6·48 |
| 13·5 | 4·84 | | | 15·2 | 13·2 |
| 15·1 | 10·0 | | | | |

ol.
12
9/60

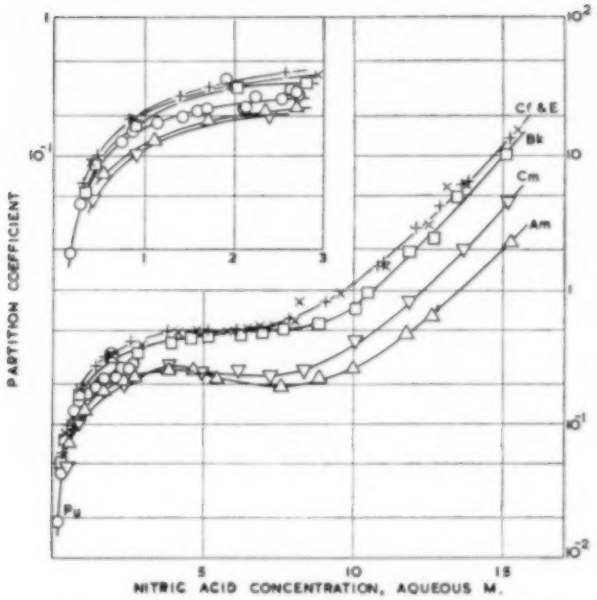



FIG. 1.—Extraction of trivalent actinides by 100% TBP.
○Pu, △Am, ▽Cm, □Bk, ×Cf, +E.

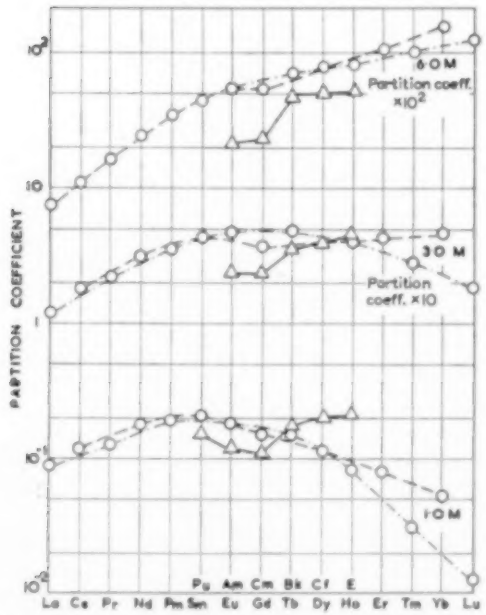

6 O M
Partition coeff. ×10²
3 O M
Partition coeff. ×10
1 O M
PARTITION COEFFICIENT
Pu Am Cm Bk Cf E
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

FIG. 2.—Partition coefficent as a function of position in the lanthanide and actinide series.
○ Lanthanides
△ Actinides

Vol. 12 1959/60

*Effect of varying the acidity*

Our experimental results using 100% TBP are given in the Table and in Fig. 1. They are in satisfactory agreement with the few results to be found in the literature.[4] It was not possible to obtain reliable results for plutonium (III) above about 2·5 M $HNO_3$ (aqueous), even in presence of sulphamate, owing presumably to oxidation

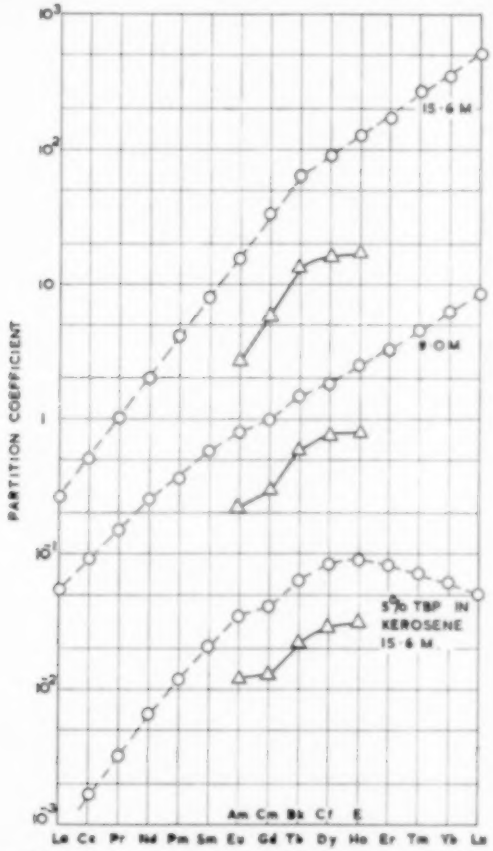



FIG. 3.—Partition coefficient as a function of position in the lanthanide and actinide series.
○ Lanthanides
△ Actinides

of plutonium; the results showed a scatter by a factor of about two in successive partitions and in forward and back partitions.

In general the results are very similar to those obtained previously for the lower lanthanides.[1] The actual values of the partition coefficients are about the same, as are also the general shapes of the curves. The gradations from element to element with increasing atomic number are, however, less regular. A particular feature which may be noted is the difficulty of obtaining a good separation of the three higher actinides (berkelium, californium and einsteinium) at *any* acidity.

[4] P. R. GRAY and S. G. THOMPSON, URCL-2069 (1952); D. F. PEPPARD, P. R. GRAY and M. M. MARKUS, ANL-WMM-989 (1953?).

*Variation of extractability with atomic number: comparison with the lanthanides*

In Figs. 2 and 3 extractability is plotted against atomic number for various conditions, with the lanthanide data[1] for comparison. The latter are fairly complex, and their full complexity is only revealed when the whole lanthanide series is studied; it would be unwise therefore to speculate too far on the basis of results for only six (and at most acidities only five) actinides.

Certain features are nevertheless noteworthy. Looking first at the data at the higher acidities ($\geqq$ 6 M $HNO_3$) we observe that the actinides are always less extractable than their lanthanide homologues, and that the difference increases with increasing acid concentration. If however we compare actinides and lanthanides of the same ionic radius (which involves, approximately, shifting the actinide curves in Figs. 2 and 3 three places to the left), then we find very similar extractabilities. Evidently, therefore, the ionic radius is a major factor in determining extractability.

We also find that curium is often less extractable than might have been expected, for instance in comparison with promethium, which has the same ionic radius. This is presumably an effect due to the 5*f*-shell in $Cm^{3+}$ being half-filled; it has already been found that gadolinium with a half-full 4*f*-shell in $Gd^{3+}$ has an anomalously low extractability.

At the lower acidities ($\leqq$ 3 M $HNO_3$) the extractabilities in the two series are generally similar, but the trends seem very different. There appears to be a minimum at curium, whereas among the lanthanides the highest partition coefficients are found in the middle of the series.

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 141 to 148. Pergamon Press Ltd. Printed in Great Britain.

# APPLICATION OF PHOSPHORIC ACID ESTERS TO THE ISOLATION OF CERTAIN *trans*-PLUTONIDES BY LIQUID–LIQUID EXTRACTION*

D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and S. MCCARTY

Argonne National Laboratory, Lemont, Illinois

(*Received* 23 *December* 1958)

**Abstract**—The use of $(GO)_2PO(OH)$ and $(GO)PO(OH)_2$ as extractants in a carrier solvent against an opposing aqueous mineral acid phase in effecting certain mutual separations in the actinide (III) series and lanthanide (III) series, including Y(III), has been investigated. The separation of Cf (and E and Fm) from Cm (and Am) by use of a di 2-ethylhexyl phosphoric acid–HCl system and the separation of Cf (and E and Fm) from Y by use of a diphenyl phosphoric acid–HCl system have been shown to be applicable to nuclear problems on a laboratory scale. It seems likely that these systems could be applied even more efficiently to large-scale operations.

The separation of Bk(III) from Ce(III) by use of a di-2-ethylhexyl phosphoric acid–HCl system and the separation of Am(III) from Pm(III) by use of a mono 2-ethylhexyl phosphoric acid–HCl system have also been demonstrated. Other systems suitable for the latter separation are reported also. No system readily applicable to the separation of Am and Cm has been developed.

The depressant effect of an alcohol on the extractive properties of $(GO)PO(OH)_2$ is noted, and the corresponding depressant effect of $(GO)_3PO$ on the extractive properties of $(GO)PO(OH)_2$ is utilized in preventing interference by the latter ester in certain separations dependent upon the extractive actions of $(GO)_2PO(OH)$.

ol.
12
9/60

DUE to the profound influence of oxidation state upon the behaviour of a given actinide or lanthanide with respect to precipitation-carrying, ion exchange (both cation and anion), and liquid–liquid extraction, mutual separations, within these groups, which are based upon differences in states of oxidation are easily effected. However, of the *trans*-plutonides, only Am[1] and Bk[2] have been reported as existing in aqueous solutions in other than the plus three state of oxidation.

Liquid–solid separations techniques have been used in the separation of Am–Cm mixtures, making use of the hexavalent state of Am[3]; and the extraction of Am(VI) from an aqueous phase into diethyl ether has been reported.[1a] The separation of Bk(IV) from lanthanides (III) and actinides (III) by preferential liquid–liquid extraction may be accomplished with high efficiency.[4] This specific technique, however, will not separate Bk from Ce; since the conditions favouring the tetravalent state of Bk also favour the tetravalent state of Ce, and Ce(IV) therefore accompanies Bk(IV).

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1a] L. B. ASPREY, S. E. STEPHANOU and R. A. PENNEMAN, *J. Amer. Chem. Soc.* **73**, 5715 (1951);
[1b] M. WARD and G. A. WELCH, *J. Chem. Soc.* 4038 (1954).
[2] S. G. THOMPSON, B. B. CUNNINGHAM and G. T. SEABORG, *J. Amer. Chem. Soc.* **72**, 2798 (1950)
[3] S. E. STEPHANOU and R. A. PENNEMAN, *J. Amer. Chem. Soc.* **74**, 3701 (1952).
[4] D. F. PEPPARD, S. W. MOLINE and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 344 (1957).

Consequently, the isolation of a given *trans*-plutonide from other actinides and lanthanides accompanying it due to its mode of formation is, in general, readily reduced to a problem involving only the trivalent state of the elements. This problem has been solved with dramatic success by use of ion exchange techniques,[5] but there exist areas in which improvement is desirable.

For example, removal of fission-product yttrium from elements 98, 99 and 100 is difficult, due to its relative ion-exchange elution position. This problem is greatly aggravated by the fact that activity-wise the yttrium contaminant exceeds the product nuclides many fold. A similar problem arises in the mutual separations: Bk(III) from Sm(III) and Am(III) from Pm(III). In addition, for ease of processing, a separation of elements of atomic number 97 and higher from relatively gross Cm (and Am) preparatory to the use of final ion exchange techniques should prove helpful.

These problems, and certain closely related ones, have been investigated from the point of view of liquid–liquid extraction, the study presently reported being restricted to extractants of the types $(GO)_2PO(OH)$ and $(GO)PO(OH)_2$ where G is an alkyl, aryl or mixed alkyl-aryl group.

## EXPERIMENTAL

### *Sources of materials*

The n-butyl, 2-ethylhexyl and para (1, 1, 3, 3-tetramethyl butyl) phenyl orthophosphoric acids were obtained as mixtures of the mono-ester and di-ester from Victor Chemical Co. and fractionated into purified mono-esters and di-esters as previously described,[6] except that the butyl esters were fractionated by use of a diethyl ether–water system. Diphenyl orthophosphoric acid was prepared and purified, as described previously,[7] using triphenyl phosphate obtained from Distillation Products (Eastman Kodak) as starting material. Tricyclo-hexyl orthophosphate was prepared by the reaction of cyclo-hexanol with phosphorus oxychloride. The purified neutral ester was then hydrolysed by heating with aqueous sodium hydroxide and dicyclo-hexyl orthophosphoric acid isolated and purified by the procedure used for the purification of di-2-ethylhexyl orthophosphoric acid. In all cases especial care was taken to ensure the absence of pyro esters, neutral esters and alcohols (or phenols).

The $\beta$-active nuclides 2·6 year $^{147}$Pm, 285 day $^{144}$Ce, and 58 day $^{91}$Y were obtained from the Isotopes Division of the Oak Ridge National Laboratory. $\beta$-active 290 day $^{249}$Bk; $\alpha$-active 18 year $^{244}$Cm, 20 day $^{253}$E and 3·4 hr $^{254}$Fm (with some accompanying 20 hr $^{255}$Fm); and fission-active 70 day $^{254}$Cf were supplied by P. R. FIELDS and A. M. FRIEDMAN of A.N.L. $\alpha$-active 470 year $^{241}$Am was obtained from A.N.L. stocks. All of these nuclides were subjected to further purification cycles, using liquid–liquid extraction techniques, before use.

### *Nomenclature*

Following the usage of PEPPARD *et al.*[8] symbolic formulae in which H represents a theoretically ionizable hydrogen and G represents an alkyl, aryl or mixed alkyl-aryl group are used. The symbols B, EH, CH, O$\Phi$ and $\Phi$ respectively represent n-butyl, 2-ethylhexyl, cyclo-hexyl, para (1, 1, 3, 3-tetramethyl butyl) phenyl—e.g. *p*-octyl phenyl, and phenyl. The symbols D and M represent di- and mono-, respectively. For example, HD$\Phi$P represents diphenyl phosphoric acid. The two type solvents, $(GO)_2PO(OH)$ and $(GO)PO(OH)_2$ are represented, respectively, as HDGP and $H_2MGP$, without regard to molecular complexity.

The distribution ratio, $K$, of a specific nuclide is defined as the concentration of nuclide in the upper divided by the concentration of nuclide in the lower of two equilibrated sensibly-immiscible

(5) R. M. DIAMOND, K. STREET, JR. and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 1461 (1954); S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN and G. T. SEABORG, *Ibid. Soc.* **76**, 6229 (1954).
(6) D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
(7) D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **7**, 231 (1958).
(8) D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and R. J. SIRONEN *J. Inorg. Nucl. Chem.* **7**, 276 (1958).

Vol. 12 1959/6

liquid phases. The effective distribution ratio, $E$, is defined as $RK$, where $R$ is the ratio of the respective volumes of the equilibrated upper and lower phases. The separation factor, $\beta$, is defined for two solutes A and B as $K_A/K_B$ and is thus also equal to $E_A/E_B$.

*Determination of distribution ratios*

In general, the distribution ratio, $K$, of a specific nuclide was determined as reported previously.[6,8] However, due to the pronounced adsorption of elements 98–100 upon glass surfaces only screening experiments were performed in glass equipment. All final data were obtained using polyethylene centrifuge cones with polyethylene stoppers permitting mixing of phases by shaking. All transfers were made with polyethylene transfer pipettes, fabricated by heating polyethylene tubing to the softening point and drawing to a fine-bore tube.

Aliquots of the separated equilibrated phases were transferred to platinum disks by means of micro-scale polyethylene weight burettes and the liquids evaporated by use of an induction heater for radiometric assay. In experiments involving both α-active Cm and fission-active Cf a correction for the α-activity associated with the Cf was made in determining the $K$ for Cm.

Unless otherwise noted, toluene was employed as the carrier diluent. All concentrations refer to equilibrated phases.

TABLE 1.—SEPARATION OF Am(III) FROM Pm:
0·50 F $H_2$MEHP–13·5 F HCL AT 2°C SYSTEM
($V$ = 2 ml, $R$ = 10, $p$ = 4, $n$ = 4, $K_{Am}$ = 0·030, $K_{Pm}$ = 0·60.
4 × $10^6$ counts/min $^{241}$Am, 6 × $10^7$ counts/min $^{147}$Pm)

| Phase | Prod. No. | Yield Am (theor.) (%) | D F (theor.) | Yield Am (obs.) (%) | D F (obs.) |
|---|---|---|---|---|---|
| Aq. | 1 | 35·0 | 8·5 × $10^2$ | 30 | >7 × $10^2$ |
| | 2 | 32·3 | 2·3 × $10^2$ | 36 | 3 × $10^2$ |
| | 3 | 18·7 | 61 | 15 | ~40 |
| | 4 | 8·6 | 16 | 7 | ~20 |

*Separations testing*

In the testing of a given separations system, unless otherwise noted, a single portion of aqueous feed (of volume $V$) was successively contacted with $p$ individual portions of organic phase (each of volume $RV$) in polyethylene tubes, each organic phase remaining in its original tube, numbered consecutively from one to $p$, beginning with one at the feed entry tube. This portion of aqueous feed was then followed, in identical sequence, by $(n-1)$ portions of aqueous "scrub" (each of volume $V$) which was identical in composition to the aqueous feed except that it was barren of the nuclides to be separated. This barren scrub and the barren organic extracting solution had been pre-equilibrated with respect to each other previously. The $n$ aqueous effluents from this assembly of tubes were numbered consecutively from one to $n$, beginning with one for the depleted aqueous feed. All transfers were made by means of polyethylene transfer pipettes.

This multiple extraction–multiple scrub method of operation, with single introduction of feed has been analysed in detail by CRAIG.[9] The general expression which was used in calculating theoretical yields (Tables 1–4) is:

$$F_{p,n} = \frac{(p+n-2)!}{(p-1)!(n-1)!}\left[\frac{E^n}{(1+E)^{(p+n-1)}}\right]$$

where $F_{p,n}$ is the fractional yield of a given solute reporting in the $p$th portion of upper phase following equilibration with $n$ portions of lower phase. The corresponding expression for $\Phi_{p,n}$, the fractional yield of the same solute reporting in the $n$th portion of lower phase following equilibration with the $p$th portion of upper phase, is readily obtained through the relation $\Phi_{p,n} = E^{-1}F_{p,n}$. Various flow-sheet tests are summarized in Tables 1–4.

[9] L. C. CRAIG, *Analyt. Chem.* **21**, 85 (1949).

TABLE 2.—SEPARATION OF Bk(III) FROM Ce(III): 0·5 F HDEHP–0·13 F HCL SYSTEM
[$V = 1$ ml, $R = 2$, $p = 4$, $n = 4$, $K_{Bk} = 3{\cdot}0$, $K_{Ce} = 0{\cdot}15$.
$2 \times 10^5$ counts/min Bk, $1 \times 10^5$ counts/min Ce (Counted as $^{144}Ce + {}^{144}Pr$)]

| Phase | Prod. No. | Yield Bk (theor.) (%) | D F (theor.) | Yield Bk (obs.) (%) | D F (obs.) |
|---|---|---|---|---|---|
| Org. | 1 | 54·0 | $1{\cdot}9 \times 10^2$ | 50 | $2 \times 10^2$ |
| | 2 | 30·8 | 35 | 35 | ~30 |
| | 3 | 11·0 | 6·6 | ~10 | >2 |
| | 4 | 3·2 | 1·2 | ~ 5 | — |

TABLE 3.—SEPARATION OF Cf FROM Y: 1·0 F HDΦP × 12·0 F HCL SYSTEM
($V = 1$ ml, $R = 3$, $p = 4$, $n = 4$, $K_{Cf} = 0{\cdot}018$, $K_Y = 7$.
$2 \times 10^5$ counts/min $^{254}Cf$, $2 \times 10^7$ counts/min $^{91}Y$)

| Phase | Prod. No. | Yield Cf (theor.) (%) | D F (theor.) | Yield Cf (obs.) (%) | D F (obs.) |
|---|---|---|---|---|---|
| Aq. | 1 | 81·0 | $2{\cdot}3 \times 10^5$ | 78 | $>10^3$ |
| | 2 | 16·6 | $1{\cdot}0 \times 10^4$ | 17 | $>10^3$ |
| | 3 | 2·13 | $5{\cdot}5 \times 10^2$ | 4 | $5 \times 10^2$ |
| | 4 | 0·22 | 29 | ~1 | ~10 |

TABLE 4.—MUTUAL SEPARATION OF Cf AND Cm: 0·75 F HDEHP + 0·22 F TEHP (IN TOLUENE)–0·25 F HCL SYSTEM
($V = 1$ ml, $R = 2$, $p = 4$, $n = 6$, $K_{Cf} = 4{\cdot}0$, $K_{Cm} = 0{\cdot}085$.
$6 \times 10^3$ counts/min $^{254}Cf$, $2 \times 10^7$ counts/min $^{244}Cm$)

| Phase and prod. | Prod. No. | Yield (theor.) (%) | D F (theor.) | Yield (obs.) (%) | D F (obs.) |
|---|---|---|---|---|---|
| Org. Cf | 1 | 49·3 | $5{\cdot}2 \times 10^4$ | 51 | $>2 \times 10^4$* |
| | 2 | 32·9 | $6{\cdot}8 \times 10^3$ | 34 | $>2 \times 10^3$ |
| | 3 | 12·8 | $8{\cdot}9 \times 10^2$ | 11 | $\sim 6 \times 10^2$ |
| | 4 | 3·8 | $1{\cdot}1 \times 10^2$ | 2 | $\sim 1 \times 10^2$ |
| Aq. Cm | 1 | 53·4 | $3{\cdot}5 \times 10^3$ | 55 | $1 \times 10^2$† |
| | 2 | 31·0 | $5{\cdot}7 \times 10^2$ | 30 | $6 \times 10^2$ |
| | 3 | 11·3 | 94 | 9 | $1 \times 10^2$ |
| | 4 | 3·3 | 15 | 4 | 7 |
| | 5 | 0·83 | 2·5 | 1 | 4 |
| | 6 | 0·19 | 0·41 | 1 | 0·3 |

* This value obtained by a re-processing of the product.
† Low value presumed due to presence of "non-extractable" Cf to perhaps the extent of 0·3 per cent.

Vol. 12 1959/6

## RESULTS

*Mutual* Am(III)–Cm(III) *separation*

In a 2·0 F HD$\Phi$P–12 F $HNO_3$ system the $K$ for Cm is 0·34 and that for Am is 0·21, the $\beta$ being 1·6. For effective separation, $R$ values greater than unity are employed, and multi-stage equipment is required. This system displays the highest $\beta$ of those studied.

In the corresponding system employing 12 F HCl, the $K$ values for Cm and Am are, respectively, 0·014 and 0·012, $\beta = 1{\cdot}2$. In the 1·5 F HDEHP–0·23 F HCl system the Cm and Am $K$ values are, respectively, 2·1 and 1·6, $\beta = 1{\cdot}3$; and in the 0·02 F HDO$\Phi$P–0·125 F $HClO_4$ system the $K$ values are approximately six, $\beta = 1{\cdot}0$.

*Separation of* Am(III) *from* Pm(III)

In both the $H_2$MEHP–HCl and $H_2$MO$\Phi$P–HCl systems, the $K$ for Pm exceeds that for Am, and the $\beta$ values increase with increasing concentration of HCl, in the concentrated HCl region. Consequently, the best separations have been achieved at reduced temperatures, since higher concentrations of HCl can thereby be maintained. For example, in the 0·90 F $H_2$MO$\Phi$P–12 F HCl system (25°C) the respective $K$ values for Pm and Am are 2·7 and 0·34, $\beta = 8{\cdot}0$. In the 0·35 F $H_2$MO$\Phi$P –14·1 F HCl system (23°C) the $K$ values are 1·55 and 0·074, $\beta = 21$, while in the same system at 2°C the $K$ values are 1·50 and 0·050, $\beta = 30$.

In the $H_2$MO$\Phi$P (in toluene)–HCl systems, severe phase disengagement difficulties are experienced. These difficulties are eliminated by substituting for the toluene diluent a diluent composed of 90 parts (by volume) of toluene and 10 parts of n-butyl alcohol. Within experimental error the $K$ values, and therefore the $\beta$ values, appear to be unaffected. The $\beta$ remains unchanged, but the $K$ values are slightly decreased by using 20 parts of n-butyl alcohol to 80 parts of toluene.

In the 0·50 F $H_2$MEHP–13·5 F HCl system (2°C), the $K$ values for Pm and Am are 0·60 and 0·030 respectively, $\beta = 20$. Although this $\beta$ compares unfavourably with the $\beta = 30$ for the 0·35 F $H_2$MO$\Phi$P–14·1 F HCl system (2°C), the system deserves consideration due to the physical ease of manipulation, no difficulties in phase disengagement being encountered. (See Table 1.)

In the systems involving a $(GO)_2PO(OH)$ type of solvent only the 2·0 F HD$\Phi$P–12·0 F HCl system (23°C) seems applicable to separations problems, the $K$ values for Pm and Am being respectively 0·14 and 0·012, $\beta = 12$. In various systems involving other examples of $(GO)_2PO(OH)$, $\beta$ values varying from eleven to eighteen are obtained, but the $K$ for Pm is too small to permit ready extraction of the more extractable element.

*Separation of* Bk(III) *from* Ce(III)

None of the systems investigated has proved outstandingly successful in effecting this separation. However, the 0·5 F HDEHP–0·13 F HCl system is usable, the $K$ values for Bk(III) and Ce(III), respectively, being 3·0 and 0·15, $\beta = 20$. (See Table 2.) In the various HDO$\Phi$P–HCl systems the $\beta$ values are below five.

*Extraction of* Y(III) *from* Cf(III), E(III) *and* Fm(III)

In the 1·0 F HD$\Phi$P–12·0 F HCl system the respective $K$ values for Y and Cf are 7·0 and 0·018, $\beta = 388$. Although the corresponding $K$ values for E and Fm are

not known precisely, they are certainly less than 0·1, so that for each of these elements the $\beta$ with respect to Y is seventy or greater. (See Table 3.) In the system, 0·40 F HDCHP–0·25 F HCl, the respective $K$ values for Y and Cf are 10·2 and 0·25, $\beta = 40$; while in the various HDBP–HCl and HDEHP–HCl systems the $\beta$ values range from twelve to twenty-five with Y invariably extracting better than Cf.

*Separation of* Cf (*and* E *and* Fm) *from* Cm (*and* Am)

No $(GO)PO(OH)_2$–mineral acid systems tested were found to be of value for this separation. Of the $(GO)_2PO(OH)$–mineral acid systems investigated, only those operating at low or moderate concentrations of mineral acid were effective, and it appears to matter little whether the acid is HCl, $HClO_4$, or $HNO_3$. However, for ease of integrating this extraction technique with the techniques of ion exchange the HCl systems seem preferable.

In the 0·075 F HDOΦP–0·60 F HCl system the respective $K$ values for Cf and Cm are 5·0 and 0·90, $\beta = 5{\cdot}5$. The corresponding values in the 0·20 F HDΦP–2·0 F HCl system are 6·5 and 0·80, $\beta = 8{\cdot}1$. In the 0·40 F HDCHP–0·25 F HCl system the $K$ values for Cf and Cm are respectively 0·25 and 0·010, $\beta = 25$. The corresponding values in the 0·25 F HDBP–0·25 F HCl system are 10·2 and 0·29, $\beta = 35$. The most promising of those investigated is the 0·75 F HDEHP + 0·22 F TEHP (toluene) –0·25 F HCl system in which the $K$ values are 4·0 for Cf and 0·085 for Cm, $\beta = 47$, the purpose of the TEHP, tri 2-ethylhexyl ortho phosphate, being to prevent interference by $H_2MEHP$ as explained in the Discussion. (See Table 4.)

In each of the foregoing systems, the $K$ for Am(III) is less than the $K$ for Cm.

Vol. 12 1959/6

## DISCUSSION

The $K$ values for the extraction of Pm(III) and Am(III) into dilute solutions of $H_2MEHP$ (or $H_2MO\Phi P$) in toluene from dilute aqueous solutions of HCl or $HClO_4$ have been shown to be directly first-power dependent upon the formality of the extractant in the toluene phase and inversely third-power dependent upon the formality of hydrogen ion in the aqueous phase.[8] These two extractants have been shown to be highly polymeric,[7] and the extraction mechanism has been postulated,[8] for the general case, as:

$$M_A^{3+} + (H_2MGP)_{x_O} \rightleftharpoons M[H_{2x-3}(MGP)_x]_O + 3H_A^+$$

it being understood that $(H_2MGP)_x$ contains an undetermined number of water molecules and that $x$ may represent an average. (The subscripts A and O refer to equilibrated aqueous and organic phases respectively.)

In systems involving $H_2MGP$ concentrations beyond 0·5 F and/or mineral acid concentrations beyond 2 F, the power dependencies depart from those noted above, and differences in lanthanide vs. actinide behaviour become more pronounced. For example, in a plot of log $K$ vs. F HCl (fixed F of $H_2MEHP$) the lanthanides (La, Pm, ...) display pronounced minima, whereas the minima for the actinides (Am, Cm) are shallow.[10] Consequently, since the $K$ for Pm lies above that for Am(III), the $\beta$ for the extraction of Pm with respect to Am(III) increases with increasing concentration of HCl in the region of high concentration. In these systems utilizing high concentrations of HCl, the operational solvent dependency is approximately first power.[10]

[10] D. F. PEPPARD, G. W. MASON and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* **10**, 147 (1959).

The phase disengagement difficulties experienced in the use of HDOΦP–HCl (conc.) systems are eliminated by substitution of n-butyl alcohol for a small portion of the toluene. However, if an alcohol is used as the sole carrier diluent, the $K$ values for both Pm and Am are depressed to such an extent that the system is unusable. For example, in the 0·35 F $H_2MO\Phi P$ (2-ethylhexyl alcohol diluent)–14·1 F HCl (2°C) system the $K$ for Pm is 0·005, to be compared with 1·5 in the corresponding system using toluene as diluent.

A similar anti-synergistic effect has been reported in a study of the extraction of Np(IV) and U(VI) from aqueous $H_2SO_4$ into a solution of $H_2MEHP$ in toluene containing $(n\text{-}C_4H_9O)_3PO$.[10] This anti-synergistic effect, presumably due to interaction of the $H_2MGP$ with the alcohol or ester, is being investigated further and will be reported in detail elsewhere.

The mechanism of extraction in the 2 F HDΦP–12 F HCl system has not been elucidated, although it has been established that the operational solvent dependency for the extraction of Pm, Am, Cf, and Y approximates third power. It has also been established that the $\beta$ values for the Pm–Am separation and the Y–Cf separation are larger in the systems employing 12 F HCl than in those employing 8 F HCl.

It is interesting to note that substitution of 12 F $HNO_3$ for 12 F HCl in the foregoing systems results in lowering the $\beta$ value for Pm with respect to Am from twelve to two, the respective $K$ values for Pm and Am being 0·40 and 0·21 in the 2 F HDΦP–12 F $HNO_3$ system. However, in this $HNO_3$–HDΦP system the $\beta$ value for the separation of Cm from Am is 1·6 as compared with a $\beta$ value of 1·2 in the corresponding HCl –HDΦP system.

A detailed study of the extraction of various actinides (III) and lanthanides (III) by HDΦP from various aqueous mineral acid phases is in progress. It has been established that at low concentrations of HDΦP and mineral acids the solvent and acid dependencies resemble those displayed by HDEHP and HDOΦP, as reported previously.[8] However, a number of points of difference remain to be reconciled.

Extraction of Am(III) and Pm in the HDEHP–HCl system, in the dilute solvent and dilute mineral acid range, has been shown[8] to be consistent with the following postulated mechanism:

$$M_A^{3+} + 3(HDEHP)_{2_O} \rightleftharpoons M[H(DEHP)_2]_{3_O} + 3H_A^+$$

Although the extraction behaviour of Ce(III) and Bk(III) in this system has not been investigated in detail, it has been shown that the predicted solvent and acid dependencies are essentially correct. Consequently, the exact conditions chosen for effecting the Bk(III)–Ce(III) separation may be varied over a considerable range with confidence. It is of interest to note that the $\beta$ for the separation of Bk(III) from Sm(III) in this system is approximately 0·4 (Sm extracting the better), although this fact is of little practical importance, since the Bk(IV)–Sm(III) separation is readily accomplished by use of a HDEHP–$HNO_3$ system reported previously.[4]

In the HDGP–HCl systems reported for the Cf–Cm separation it is assumed that the mechanism of extraction is similar to that indicated in the preceding discussion. The $\beta$ value of forty-seven (respective $K$ values 4·0 and 0·085 for Cf and Cm) found for the 0·75 F HDEHP + 0·22 F TEHP (toluene)–0·25 F HCl system makes this an attractive system even for small-scale nuclear separations in which multiple extraction with multiple scrubbing is not a simple technique, since only a few stages are, in general, required.

In this system, the TEHP does not enhance $K$ values or the $\beta$ value but does prevent interference by any $H_2$MEHP which might be formed from the HDEHP by hydrolysis. Conversion of only a few per cent of the HDEHP into $H_2$MEHP results in a solvent with very poor discriminating properties, the $K$ for Cm approaching that for Cf. Through anti-synergistic interaction the TEHP inactivates the $H_2$MEHP without appreciably affecting the action of HDEHP. Since some hydrolysis is likely to occur in a high intensity radiation field, such a precautionary measure is desirable.

The value of selected examples of the systems discussed, in the field of separations chemistry, is demonstrated in the Tables pertaining to flow sheet testing. The separation of Cf from Y contaminant (Table 3) is easily accomplished. If D.F. values in excess of those tabulated are required it is desirable to extract both Cf and Y into 0·75 HDEHP (toluene) from 0·1 F HCl for the purpose of eliminating any small fraction of non-extractable Y. This extract is then contacted with 12 F HCl; and the re-extract, following contacting with toluene to remove traces of HDEHP, is treated as feed for the 1·0 F HDΦP–12 F HCl system.

The separation of Cf from Cm (Table 4) by use of the 0·75 F HDEHP + 0·22 F TEHP (toluene)–0·25 F HCl system, while not so strikingly efficient as the Cf–Y separation (Table 3), is sufficiently effective to make this technique a valuable adjunct to the technique of ion exchange. With the hope of improving upon this separation, i.e. devising a system with a more favourable $\beta$, a series of phosphonates are being synthesized for testing; since these compounds with a C—P bond should possess extraction characteristics differing considerably from those of the ortho phosphates.

The separation of Bk(III) from Ce(III), through use of the 0·5 F HDEHP–0·13 F HCl system (Table 2) is reasonably efficient. However, this technique appears to offer no advantages over those involving ion exchange.

Use of the 2·0 F HDΦP–12·0 F HCl system for the separation of Am(III) from Pm appears promising. The various $H_2$MGP–HCl systems display larger $\beta$ values, but the difficulty of maintaining HCl concentrations in the 13–14 F range, and the inconvenience of operating at temperatures lower than room temperature make the systems seem less desirable. However, in certain separations problems one of these systems might be preferred. (See Table 1 for illustrative separations data.)

The Am–Cm separation problem has not been successfully solved through study of these systems. It seems likely that any highly efficient liquid–liquid extraction separation of this pair of elements must utilize one of the oxidized states of Am. At present the extraction behaviour of Am(VI)[1] in various HDGP (and $H_2$MGP)–oxidizing mineral acid systems is being investigated. The application of such systems to mutual separation of Am and Cm has, to date, been defeated by the instability of Am(VI) in exceedingly dilute solutions. Consequently, although an Am product free from Cm can be obtained by such techniques, a Cm product free from Am cannot be.

With the possible exception of the $H_2$MGP–HCl systems, all of the systems described are amenable to counter-current operation in which products of constant composition are removed continuously or pseudo-continuously. In an automatic counter-currently operating system the $\beta$ value of 12 (2·0 F HDΦP–12 F HCl at 23°C) is sufficiently large to permit ready mutual separation of Am(III) and Pm(III).

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 149 to 153. Pergamon Press Ltd. Printed in Great Britain.

# THE COMPLEXING OF TETRAVALENT URANIUM WITH DIALKYLPYROPHOSPHORIC ACID

D. GRDENIĆ
Laboratory for General and Inorganic Chemistry,
Faculty of Science, University, Zagreb

and B. KORPAR
Department for Structural and Inorganic Chemistry,
Institute Rudjer Bošković, Zagreb

(*Received* 23 *February* 1959)

**Abstract**—The extraction of uranium (IV) ions into a ligroin solution of dialkylpyrophosphoric acid from aqueous sulphuric acid solution has been investigated. It has been established that the extractable species is a complex compound defined by formula $U(R_2HP_2O_7)_4$. It may be considered as an addition product of two molecules of the reagent to one molecule of uranium (IV) dialkylpyrophosphate. The uranium (IV) dialkylpyrophosphates $U(R_2P_2O_7)_2$ for R = ethyl, i-propyl, n-butyl, n-octyl were also isolated as green powders insoluble in water, acids and organic solvents but soluble in dialkylpyrophosphoric acid solutions. The properties of the compounds described have been explained by assuming that in their structure uranium occurs in co-ordination eight.

ol.
12
9/60

DIOCTYLPYROPHOSPHORIC acid (symbolized as OPPA) dissolved in kerosene has been very successfully used by LONG *et al.*[1] for the recovery of uranium by solvent extraction from sulphuric acid leaches of phosphate ores with a relatively small uranium content. The main point of their method consists in the reduction of uranyl-to U(IV)-ion whereby an increase of the extraction coefficient for about twenty times has been attained. The authors believed that the extraction proceeded under the formation of U(IV)-dioctylpyrophosphate with the uranium atom in a six-membered chelate ring, but they have not taken any further investigation in this direction.

The present investigation has been particularly devoted to the question of the extractable species in the case of solvent extraction of U(IV)-ions by means of dialkylpyrophosphoric acids. This question should be considered as a part of a general problem on the co-ordination properties of uranium. Its solution is of interest (i) for the stereochemistry of uranium and (ii) for the estimation of the relative affinity of ligand atoms in complexing agents to uranium ion.

The problem of the co-ordination chemistry of uranium has been reviewed by COMYNS[2] and a discussion on the relative affinity of the ligand oxygen atoms in phosphorylated reagents has been given recently by KENNEDY.[3] The great majority of papers published up to now treat these questions only in the case of uranyl-ion.

(1) R. S. LONG, D. A. ELLIS and R. H. BAILES, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 8, p. 77. United Nations, New York (1956).
(2) A. E. COMYNS, *The Co-ordination Chemistry of Uranium: A Critical Review*, AERE C/R-2320 (1957).
(3) J. KENNEDY, *Chem. & Ind.* 950 (1958)

However, it has been recently established by means of X-ray analysis that the co-ordination polyhedron of oxygen atoms in Th(IV)-acetylacetonate is a square antiprism.[4] Such a co-ordination apparently occurs also in U(IV)- and Ce(IV)-acetylacetonates since the isomorphism of these compounds has been proved by means of crystallographic and X-ray measurements.[5]

It is quite sure, therefore, that uranium in the U(IV)-dioctylpyrophosphate has a co-ordination number eight effectuated in the same co-ordination polyhedron, i.e. square antiprism. In this case all the four phosphoryl oxygen atoms would be co-ordinated to uranium and a particular inner phosphatocomplex would occur (Fig. 2a). A proof for the existence of such a complex would be of importance in treating ato-complexes, especially in the actinide series. The same question has been previously treated in the case of lanthanides by PEPPARD *et al.*[6] For this reason the present investigation was undertaken with the aim to isolate the U(IV)-dialkylpyrophosphates, which were supposed by LONG *et al.*,[1] in order to establish whether they really occur in organic phase in the course of extraction.

## RESULTS AND DISCUSSION

When ethanol was added to the solution which had been obtained by extracting acid aqueous solution of U(IV) sulphate with an OPPA–ligroin solution, a green precipitate was produced. The precipitate had the composition of a pure U(IV)-dioctylpyrophosphate defined by formula $U(Oct_2P_2O_7)_2$. Surprisingly, it was completely insoluble in ligroin as well as in all common organic solvents. Consequently, U(IV)-dioctylpyrophosphate could not be considered as the extractable species. It was assumed therefore that for the solvent extraction of U(IV)-ion with OPPA an excess of the latter was necessary. This assumption was immediately confirmed since U(IV)-dioctylpyrophosphate was easily soluble in a OPPA–ligroin solution. Apparently, the extractable species is a ligroin soluble complex of U(IV)-dioctylpyrophosphate with OPPA. This complex dissociates in ethanol owing to the great solubility of OPPA in alcohol, so that insoluble U(IV)-dioctylpyrophosphate is precipitated.

The solubility of dialkylpyrophosphoric acid with lower alkyls in water is sufficiently high so that U(IV) complex with diethyl- or dipropylpyrophosphoric acid in ligroin dissociated even in contact with water by precipitating insoluble green U(IV)-diethyl- or dipropylpyrophosphate. This precipitation occurred always in the course of extraction of an U(IV)-sulphate solution with diethyl- or dipropylpyrophosphoric acid in ligroin.

The dissolution of U(IV)-dialkylpyrophosphate in an excess of reagent follows a constant and well defined ratio. It has been proved that always for the dissolution of one mole of uranium salt two moles of dialkylpyrophosphoric acid are necessary. When OPPA–ligroin solution saturated with U(IV)-ions was evaporated under reduced pressure, a green viscous mass remained of a defined composition for which formula $U(Oct_2HP_2O_7)_4$ was established by analysis. This compound was easily soluble in ligroin producing a green solution. From this solution ethanol again precipitated the insoluble U(IV)-dioctylpyrophosphate.

[4] D. GRDENIĆ and B. MATKOVIĆ, *Nature, Lond.* **182**, 465 (1958).
[5] D. GRDENIĆ and B. MATKOVIĆ, *Acta Cryst.* In press.
[6] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957)

The same formula $U(Oct_2HP_2O_7)_4$ for the complex has also been obtained by determination of the uranium content in a saturated ligroin phase. The experiment was carried out with OPPA–ligroin solutions of different concentration (Fig. 1). The saturation concentration of U(IV)-ion in the ligroin phase is a linear function of the reagent concentration [OPPA]. The points which were obtained experimentally

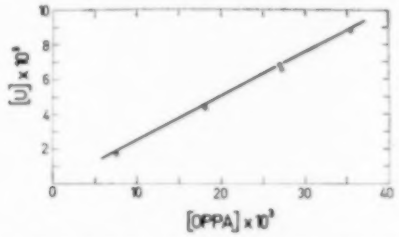



FIG. 1.—Saturation concentration of uranium (IV) in ligroin phase [U] plotted vs. concentration of dioctylpyrophosphoric acid in ligroin [OPPA]. The experimental points lie almost exactly on a straight line with the slope of 1/4 thus proving the formation of complex $U(Oct_2HP_2O_7)_4$ in the solvent phase.

by varying OPPA-content in ligroin from 0·5–2 per cent, tallied well with a straight line with the slope of 1/4. It is therefore beyond any doubt that the extractable species in solvent extraction of U(IV)-ions with dialkylpyrophosphoric acid is a complex with formula $U(Alk_2HP_2O_7)_4$.

Vol. 12 59/60

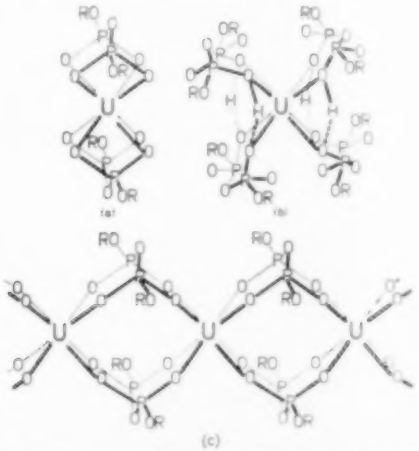


FIG. 2.—Complexing of uranium (IV) by dialkylpyrophosphoric acid: (a) U(IV)-dialkylpyrophosphate monomer which has not been isolated and apparently does not exist; (b) Soluble complex of U(IV)-dialkylpyrophosphate with dialkylpyrophosphoric acid, one of possible formulae; (c) Insoluble U(IV)-dialkylpyrophosphate polymer. (A cube instead of a square antiprism for co-ordination polyhedron is drawn for the sake of simplicity.)

The fact that U(IV)-dialkylpyrophosphorates are insoluble in all organic solvent) indicates that they have not a simple monomeric structure as given by formula (as in Fig. 2, but it is much more likely that they are polymers. It may be expected that

owing to the inner strain in the structure (a), the phosphoryl oxygens do not co-ordinate with their "own" uranium but enter into the co-ordination sphere of adjacent uranium atom, thus producing a polynuclear complex which may be depicted by formula (c) in Fig. 2. The phosphoryl oxygen bridges in this structure are sufficiently resistant to the action of water, acids and other solvents, but they break under the action of a suitable complexing agent, as for example OPPA itself, giving monomeric complex $U(Alk_2HP_2O_7)_4$ soluble in lingroin.

With the assumption of a co-ordination number eight for uranium, several different formulae can be written down for this complex. In Fig. 2, one of these is shown (b) in which the hydrogen atoms bridge over the ligand oxygen atoms. The choice of this formula is entirely arbitrary and it is not insisted in any way upon it. For the sake of simplicity a cube instead of a square antiprism has been drawn as co-ordination polyhedron for uranium in the formulae (a)–(c), since it is not essential for the present discussion.

The stability of the complex $U(Alk_2HP_2O_7)_4$ is very low since the addition of alcohol to its ligroin solution precipitates immediately polymeric U(IV)-dialkylpyrophosphate. The solvation energy of dialkylpyrophosphoric acid in alcohol exceedes therefore the energy of formation of the complex from nonsolvated acid (as it is in ligroin) with U(IV)-dialkylpyrophosphate. Besides the energy is gained by the polymerization over phosphoryl-oxygen bridges so that insoluble polymeric U(IV)-dialkylpyrophosphate is the most stable species. This conclusion is also supported by the reaction

$$U(R_2HP_2O_7)_4 + U^{4+} \rightarrow 2\ U(R_2P_2O_7)_2 + 4\ H^+ \qquad (1)$$

which occurred always by prolonged contact of the uranium saturated ligroin phase with an aqueous solution of $U(SO_4)_2$. This reaction was taken into account in the course of the determination of the ratio given in Fig. 1 by limiting the duration of of the contact between the ligroin and the aqueous phase.

Vol. 12 1959/6

## EXPERIMENTAL

*Preparation of the reagents.* Tetravalent uranium was used in the form of uranium (IV) sulphate solutions which were always prepared before experiment by dissolving tetrahydrated salt in diluted (5–15 per cent) sulphuric acid. Water, redistilled in nitrogen atmosphere, was used. Uranium (IV) sulphate tetrahydrate was obtained by cathode reduction of analytical grade uranyl sulphate.

OPPA solution in ligroin (b.p. 80–110°C) were prepared according to the instruction given by LONG *et al.*[1] To a suspension of reagent grade phosphorus pentoxide (0·1 mole) in ligroin (100 ml)/n-octanol/0·2 mole) was slowly added under reflux. The solution was then heated for half an hour at 70°C, diluted with ligroin to the necessary concentration of the reagent (usually to 2 per cent), and filtered in order to remove the slight impurities originated from phosphorus pentoxide. Ligroin solutions of diethyl-, di-i-propyl- and di-n-butylpyrophosphoric acid were prepared in the same way.

The OPPA–solution prepared in the manner described above contained a little octanol which by itself acts as an extractant. For this reason, octanol was removed from the reagent before it was used for the experiment on the determination of $U^{4+}$–OPPA ratio in the extractable species. For this purpose, the original solution was evaporated, under reduced pressure (16 mm), the traces of octanol distilled off *in vacuo* (0·5 mm) at 70°C. The syrupy residue which did not contain free octanol any more, was again dissolved in ligroin to the proper concentration.

*Analytical.* For the uranium determination the sample of dialkylpyrophosphate was decomposed by sodium hydroxide solution (10%), uranium (IV) oxide filtered off, washed with hot water and dissolved in diluted (30 per cent) nitric acid. The solution was neutralized with ammonia (10 per cent) uranyl-ion precipitated with oxine solution, the precipitate ignited to $U_3O_8$ and weighed.

For the analysis of phosphorus the sample was decomposed by using Carius method, phosphoric acid separated by precipitation with ammonium molybdate and then determined gravimetrically as $Mg_2P_2O_7$. Carbon and hydrogen were determined by micro-combustion.

The concentration of uranium (IV) sulphate solutions was determined by titration with potassium permanganate solution.

*Uranium* (IV) *di-n-octylpyrophosphate.* A solution (50 ml) of uranium (IV) sulphate (with 1% U content) and ligroin solution (5 ml) of di-n-octylpyrophosphoric acid (2 per cent) were placed in a separate funnel and shaken for 3 min. The liquids were separated and then ethanol (50 ml) was added to the intense green ligroin solution. The precipitate was filtered off, washed with ethanol and ethyl ether and dried at 130°C. It is a pale green powder, insoluble in water and organic solvents, indifferent to mineral acids, but easily soluble in OPPA–ligroin solution. It decomposes at about 245°C. (Found: U, 22·61; P, 11·72: C, 36·63; H, 6·75. Calc. for $C_{32}H_{64}O_{14}P_4U$: U, 22·93; P, 11·94; C, 37·00; H, 6·55%.)

*Uranium* (IV) *di-i-propylpyrophosphate.* A solution (100 ml) of uranium (IV) sulphate (containing 1%U) in diluted sulphuric acid (10 per cent) was shaken with 10 ml of a 2 per cent benzene solution of di-i-propylphosphoric acid (10 ml). The pale green precipitate which fell down in the aqueous phase, was filtered off, washed with ethanol and ethyl ether. It is insoluble in water, acids and organic solvents but soluble in the excess of the reagent. It decomposes at 230°C. (Found: U, 31·14; C, 19·03; H, 4·21%. Calc. for $C_{12}H_{28}O_{14}P_4U$: U, 31·04; C, 18·99; H, 3·72%.)

*Uranium* (IV) *di-n-butylpyrophosphate and uranium* (IV) *diethylpyrophosphate.* These compounds were prepared in a similar way. The ethyl derivates precipitated in the course of extraction, fell down in the aqueous phase and was isolated as it has been described for propyl-derivate. The butyl derivate was separated in the same way as octyl-derivative. Both compounds are pale green powders insoluble in water, acids and organic solvents, but soluble in ligroin solution of the reagent or OPPA.

*Isolation and determination of the complex in ligroin phase.* A solution (100 ml) of uranium (IV) sulphate (containing 0·2% U) in 10 per cent sulphuric acid was extracted with 2 per cent ligroin solution (10 ml) of di-n-octylpyrophosphoric acid, which was liberated from free octanol as already described. The extraction was carried out in a separatory funnel by applying light shaking for 10 min. Ligroin phase, which after this time was saturated with uranium, was separated and evaporated under reduced pressure. The deep green residue was dried at 60°C *in vacuo* (0·3 mm). The product was a viscous mass, easily soluble in ligroin. (Found: U, 11·55%. Calc. for $C_{32}H_{72}O_{28}P_8U$: 12·92%.)

The existence of the compund $U(Oct_2HP_2O_7)_4$ as the extractable species was proved also by extraction of $U(SO_4)_2$–solutions with a higher uranium content than necessary for the saturation of solvent phase. The extractions were carried out with OPPA–solutions of different concentrations, i.e. 0·5, 1·0, 1·5 and 2·0 per cent approximately. The uranium (IV) sulphate solutions in 15 per cent sulphuric acid had concentrations from twice to tenfold than necessary for the saturation of the ligroin phase. The extraction was carried out by applying light rocking for 10 min. By vigorous shaking or under prolonged contact of the phases, after the saturation of solvent phase, the reaction given by (1) occurred. The results of the experiment are given in Fig. 1. The saturation was always reached at a ratio 1 : 4 of gramme atom of uranium to gramme mole of OPPA.

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 154 to 173. Pergamon Press Ltd. Printed in Great Britain.

# NITROSYLRUTHENIUM NITRATO COMPLEXES IN AQUEOUS NITRIC ACID

J. M. FLETCHER, P. G. M. BROWN, E. R. GARDNER,
C. J. HARDY, A. G. WAIN and J. L. WOODHEAD
Chemistry Division, Atomic Energy Research Establishment, Harwell, Didcot, Berks

(*Received* 27 *February* 1959)

**Abstract**—Paper chromatographic and ion exchange studies of nitrosylruthenium nitrato complexes in 0·1–14·5 M nitric acid have enabled the complexes to be separated into four groups in order of increasing complexing from the mononitrato to the pentanitrato complex, $H_2RuNO(NO_3)_5$. The eleven nitrato complexes which can be formulated assuming a regular octahedral arrangement around the hexa-co-ordinated ruthenium have been allocated to these groups. Absorption spectra and compositions are presented for equilibrium mixtures of the complexes in nitric acid and the successive formation constants for nitrato complexing of nitrosylruthenium have been calculated. Other measurements include the rates of one of the denitration reactions at 0° and 25° and the ruthenium distribution coefficients after prolonged contact of solutions in 0·5–10 M nitric acid with an anion exchange resin. In contrast to other metal nitrates, tributyl phosphate extracts preferentially the tetra- and pentanitrato acids rather than the uncharged trinitrato complex.

Vol
12
1959/

A PREVIOUS paper on nitrosylruthenium complexes[1] described methods of obtaining mixtures of the nitrato complexes and reported some of their properties. The solutions were regarded as containing a series of mononuclear aquo-hydroxy complexes of general formula $[RuNO(NO_3)_y(OH)_{3-y}(H_2O)_2]$, from which some of the lower nitrato members condensed to polynuclear forms. Although completely hydrolysed at a pH greater than 2 the complexes are stable in more concentrated acid; accordingly their individual properties have been studied in 0·1–15 M nitric acid.

Hitherto we have thought the trinitrato complex, $[RuNO(NO_3)_3(H_2O)_2]$, to be the most fully nitrated complex normally present in nitric acid solution. This belief was based[1] on our isolation of solids containing, on an average, three nitrato groups per ruthenium atom and on our failure to prepare salts from such possible anions as $[RuNO(NO_3)_5]^{2-}$. The four species identified by distribution methods (solvent extraction and paper chromatography) were accordingly considered[2,3,4] to be the tri-, di-, mono- and non-nitrato (possibly polymeric) complexes respectively.

Our present results show that the earlier interpretation was an over-simplification. There is strong evidence that anionic complexes, analogous to $[RuNOCl_5]^{2-}$ in the

[1] J. M. FLETCHER, I. L. JENKINS, F. M. LEVER, F. S. MARTIN, A. R. POWELL and R. TODD, *J. Inorg. Nucl. Chem.* **1**, 378 (1955).
[2] A. G. WAIN, P. G. M. BROWN and J. M. FLETCHER, *Chem. & Ind.* 18 (1957).
[3] P. G. M. BROWN, J. M. FLETCHER, C. J. HARDY, J. KENNEDY, D. SCARGILL, A. G. WAIN and J. L. WOODHEAD, *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Vol. 17, p. 118. United Nations, New York (1959).
[4] J. M. FLETCHER, *J. Inorg. Nucl. Chem.* **8**, 277 (1958).

chloro series, containing more than three nitrato groups per ruthenium atom, exist in nitric acid solutions even though further efforts to isolate their salts with caesium and with cobaltic cyclo-pentadiene have failed. The solids derived from the nitric acid solutions[1] were obtained by evaporation under reduced pressure at room temperature because the complexes oxidise to ruthenium tetroxide at higher temperatures. Agents such as caustic potash, which were present during the evaporation, will have tended to hydrolyse such ions as $[RuNO(NO_3)_5]^{2-}$ with the liberation of nitric acid during the slow concentration procedure. The glassy nature of the solids so produced suggests they were mixtures in which we believe that the trinitrato complex was probably the predominant species, and that there were also present roughly equivalent amounts of the lower and higher nitrato complexes. In one of several preparations an average of 3·25 rather than 3 nitrato groups per ruthenium atom was found.

There does not appear to be detectable polymer formation in aqueous solutions which are more than 0·2 M in $HNO_3$ and less than $10^{-2}$ M in Ru. The spectra in the near ultra-violet of solutions within this range of concentration are very similar and the distribution coefficient of ruthenium between aqueous and organic phases is independent of the total Ru concentration. This coefficient would be expected to be changed by polymer formation.

Paper chromatograms of solutions in 3–15 M $HNO_3$, previously aged to reach equilibrium, enable the complexes to be divided into four Groups:

| Group | $R_f$ value with elution by methyl isopropyl ketone (MIPK) | $R_f$ value with elution by dibutyl cellosolve (DBC) |
|---|---|---|
| A | <0·1 | <0·2 |
| B | ~0·25 | <0·2 |
| C | 0·4–0·9 | <0·2 |
| D | >0·9 | 0·2–0·7 |

Chromatographic examination of solutions before and after ion exchange treatment shows that complexes in Group D are strongly adsorbed by anion exchange resins, and those in Groups A and B are preferentially adsorbed by cation exchange resins.

Assuming octahedral co-ordination around a ruthenium atom the several nitrato complexes of (RuNO) III shown in Table 1 are possible with OH or $H_2O$ as the other ligands. These can be divided into complexes which (i) have and (ii) do not have a nitrato group *trans* to the (NO) group. The *trans*-, or 6-position in our nomenclature, is unique in being most remote from the electronic disturbances caused by the nitrosyl group and is often occupied by a hydroxyl group in other RuNO complexes, e.g. $[RuNO(NO_2)_4OH]^{2-}$ [1] and $[RuNOCl_4OH]^{2-}$.[5] We have accordingly assumed that the position is occupied by -OH, rather than by $H_2O$, when it is not occupied by a nitrato group. The correlation which we suggest between the hypothetical complexes and those we have observed is indicated in Table 1.

[5] N. A. Parpiev and G. B. Bobii, *Zh. Neorg. Khim.* **2**, 1972 (1957).

TABLE 1.—POSSIBLE RuNO NITRATO COMPLEXES

| Group in position 6* | RuNO complex | Position* of nitrato groups | Formula | Suggested correlation with groups found by chromatography |
|---|---|---|---|---|
| | | | | Group |
| A nitrato group | Mononitrato | 6 | $[RuNO{\cdot}NO_3(H_2O)_4]^{2+}$ | A |
| | Dinitrato | 2–6 | $[RuNO(NO_3)(H_2O)_3]^{+}$ | B |
| | Trinitrato | 2–3–6 | $[RuNO(NO_3)_3(H_2O)_2]$ | C |
| | Trinitrato | 2–4–6 | | |
| | Tetranitrato | 2–3–4–6 | $[RuNO(NO_3)_4H_2O]^{-}$ | D |
| | Pentanitrato | 2–3–4–5–6 | $[RuNO(NO_3)_5]^{2-}$ | D |
| Not a nitrato group | Mononitrato | 2 | $[RuNO{\cdot}NO_2OH(H_2O)_3]^{+}$ | A |
| | Dinitrato | 2–3 | $[RuNO(NO_3)_2OH(H_2O)_2]$ | B |
| | Dinitrato | 2–4 | | |
| | Trinitrato | 2–3–4 | $[RuNO(NO_3)_3OH{\cdot}H_2O]^{-}$ | C |
| | Tetranitrato | 2–3–4–5 | $[RuNO(NO_3)_4OH]^{2-}$ | D |

* Based on the arrangement


## 1. EXPERIMENTAL

(a) *Stock solutions of nitrosylruthenium nitrato complexes in nitric acid*

$^{106}Ru$ labelled solutions ($\sim 10^{-7}$ M in Ru) of RuNO nitrato complexes in $\sim$12 M $HNO_3$, from R.C.C., Amersham, were used to prepare other stock solutions of higher ruthenium concentration by adding to them nitrosylruthenium hydroxide, $RuNO(OH)_3$. The mixture was refluxed in 8–14 M $HNO_3$ for not less than an hour, since 30 min had been found to be insufficient for complete depolymerization, and rapidly cooled to room temperature.

Solutions of the nitrato species at equilibrium in dilute nitric acid remain stable for long periods provided light and air are excluded; air causes slow oxidation to RuIV polymer (the form of RuIV common to solutions in perchloric, nitric and hydrofluoric acids) and a marked increase in absorption over the wavelength range 330–580 m$\mu$. Absence of the polymer was assured by spectrophotometric measurements at 480 m$\mu$ where its molar extinction coefficient ($\epsilon$) differs from that of the RuNO nitrato complexes by a factor of about ten over a wide range of nitric acid concentration. Typica values of $\epsilon$ are given in Table 2 (see also Fig. 1).

TABLE 2.—MOLAR EXTINCTION COEFFICIENTS AT 20°C FOR RUTHENIUM SOLUTIONS AT EQUILIBRIUM IN NITRIC ACID

| Complexes | 330 | 350 | 370 | 390 | 410 | 430 | 450 | 470 | 480 m$\mu$ |
|---|---|---|---|---|---|---|---|---|---|
| *RuNO nitrato | 142 | 118 | 96 | 82 | 72 | 70 | 74 | 78 | 67 |
| *RuIV polymer | 1830 | 1630 | 1370 | 1120 | 930 | 830 | 785 | 790 | 790 |
| †RuNO nitro | 534 | 298 | 137 | 76 | 61 | 60 | 45 | 33 | 30 |

* In 3 M nitric acid

† A typical synthetic mixture made by adding nitrous acid to an equilibrium mixture of RuNO nitrato complexes in 1 M nitric acid.

Vol. 12 1959/6

Nitro complexes of RuNO, formed by the action of nitrous acid, can also occur in these stock solutions either from minor variations in their method of preparation, e.g. slow cooling after boiling, or from the formation of nitrous acid *in situ*. As they cause a marked increase in the optical density at wavelengths below 350 mμ (Table 2), they can be detected by spectrophotometry under certain conditions, for instance in solutions with Ru $> 10^{-3}$ M in relatively low nitric acid concentrations. Their presence is also shown by anomalous results from paper chromatography.[3] Their formation can be prevented by adding urea.

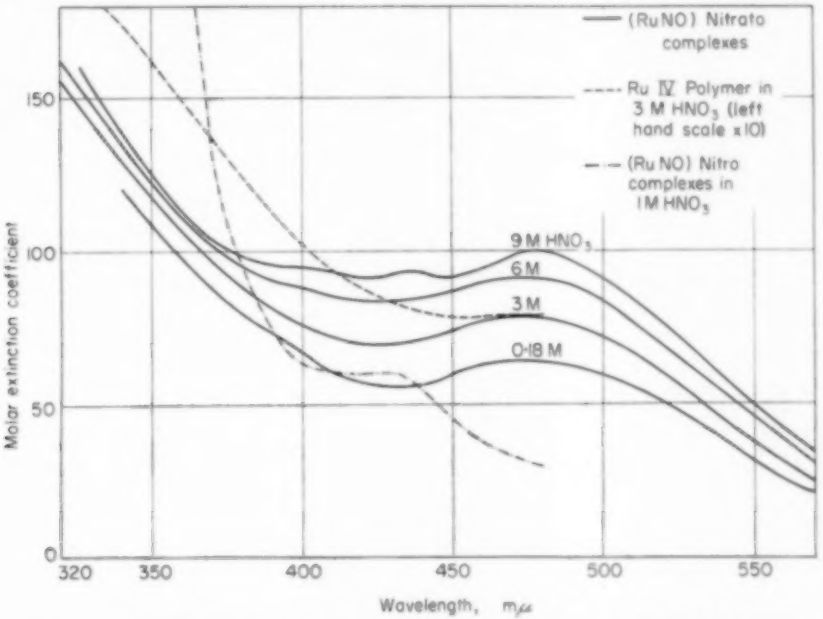



FIG. 1.—Absorption spectra at ~20°C of equilibrium mixtures of RuNO nitrato complexes (~$10^{-2}$ M) in nitric acid and of likely impurities (see Table 2). The curve for 1 M $HNO_3$ is similar to that for 0·18 M $HNO_3$.

(b) *Organic solvents*

Tributyl phosphate (TBP) was purified by steam distilling the commercial material in the presence of dilute sodium hydroxide, and washing it with aqueous sodium carbonate and then with water or 0·1 M nitric acid. The product was dried under vacuum and diluted with dry odourless kerosene to give solutions nominally 5, 10, 15, 20 and 30% TBP by volume. When equilibrated with aqueous nitric acid, the concentration of TBP falls, for example, from 20% to 19·5% solution.

B.D.H. "Laboratory Reagent" methyl isopropyl ketone (MIPK) and dibutyl cellosolve (DBC) were used without further purification.

(c) *Distribution measurements with organic solvents*

The organic solvent was pre-equilibrated with the relevant aqueous phase. Except when otherwise stated, the organic and aqueous phases were stirred together for 30 sec at 0°C, centrifuged and analysed. There was no significant difference in the ruthenium distribution on varying the stirring time from 10–45 sec. The relative concentrations of ruthenium in the organic and aqueous phases were determined by liquid-counting of the rhodium daughter, using a γ-scintillation counter fitted with a 20 mg/cm² lead-aluminium absorber.

(d) *Paper chromatography*

The technique was similar to that previously described[2] but to give improved resolution, small aliquots, usually 1 μl., though sometimes 5 μl. with solutions in dilute acid, were applied. The

eluting solvents, MIPK or DBC, were each conditioned with 3 M $HNO_3$, and the DBC was centrifuged after conditioning. Whatman No. 1 or 41 (type CRL/1) paper was used and strips were marked to give 17 × ½ cm sections, the sample being placed as a band on the bottom section. Times for elution to the top of the strip at about 20°C were for Whatman No. 1 paper about 23 and 42 min, and for Whatman No. 41 paper about 13 and 27 min for MIPK and DBC respectively. The 17 sections (numbered 1–17 with No. 1 being that on which the sample had been placed) were cut out, separately mounted on aluminium trays, and $\beta$ or $\gamma$ counted; $\beta$ counting, through a 6·3 mg/cm² aluminium absorber, was preferred with low levels of activity because of the lower background and higher counting rate.

TABLE 3.—RELATIVE MOLE PERCENTAGES AT EQUILIBRIUM AT 20°C

| $HNO_3$ | By DBC elution Group D | By MIPK elution Group A | B | C | D | By solvent extraction Group C | D |
|---|---|---|---|---|---|---|---|
| 0·11 M | | 96% | 4% | | | | |
| 1·0 | | 65 | 19 | 13% | 2·5% | | |
| 2·0 | 3·5% | | | | | | |
| 3·0* | 8† | 34 | 33 | 24 | 9 | 15% | 7% |
| 4·5* | 19·5 | 27 | 28 | 26 | 19 | 20 | 18 |
| 7·5 | | 9 | 22 | 23 | 46 | 19 | 42 |
| 7·7 to 8·0* | 47 | 8 | 20 | 23 | 49 | | |
| 9·6 | 54 | | | | | 20 | 55·5 |
| 12·0 to 12·6* | 70 | 4·5 | 10 | 16 | 69·5 | | |
| 14·5 | 70 | 4 | 6 | 14 | 76 | 13 | 81 |

* For DBC and MIPK elutions, values given are the average of several results.
† 16 per cent at 100°C.

To obtain good resolution with DBC elutions at section 3, and reproducible results in spite of varying laboratory humidity, the paper was dried with hot air from a hair-dryer, before the sample was placed on it. The strips were eluted immediately following the addition of the sample since its drying on the paper before elution impairs the resolution.

Since nitric acid at high concentration may attack the eluting solvent and the paper, the behaviour of such acid solutions was tested both by application to the paper at the existing acidity and also immediately after rapid dilution to 3 M $HNO_3$. With DBC elution in particular, failure to reduce the acidity when it was above 10 M led to inconsistent results and poor resolution; dilution to 3 M $HNO_3$ immediately prior to their examination was therefore adopted for such solutions and was also frequently used for solutions in 4–10 M $HNO_3$. Tests (Fig. 7 gives results for 25°) showed that equilibrium was not significantly changed by the dilution procedure provided ageing after dilution did not exceed a few minutes.

(e) *Ion exchange resins: pretreatment and use*

Batches of 50 $\mu$ diameter DeAcidite-FF resin in the $Cl^-$ form, and Zeokarb 225 resin in the $Na^+$ form, were converted to their respective $NO_3^-$ and $H^+$ forms. For this purpose 20 g of the anion resins was stirred for 1 hr in 600 ml of a dilute solution of ammonia; the supernatant was decanted and the resin washed with water. It was successively stirred for periods of 1 hr with 1 M $HNO_3$, 2 M $HNO_3$ and 6 M $HNO_3$ (three times), and stored under dilute $HNO_3$. The cation resin was washed once with water, twice with 1 M $HNO_3$, three times with 6 M $HNO_3$ and stored under 6 M $HNO_3$.

To measure the adsorption of ruthenium species and to obtain the distribution coefficient the wet resin was washed twice with nitric acid of the appropriate concentration, centrifuged and its volume measured. The supernatant acid was discarded, the ruthenium solution added to the resin and stirred for a few minutes, and aliquots of the solution were removed through a small glass-wool filter at the end of the pipette and $\gamma$ counted.

Vol. 12 1959/6

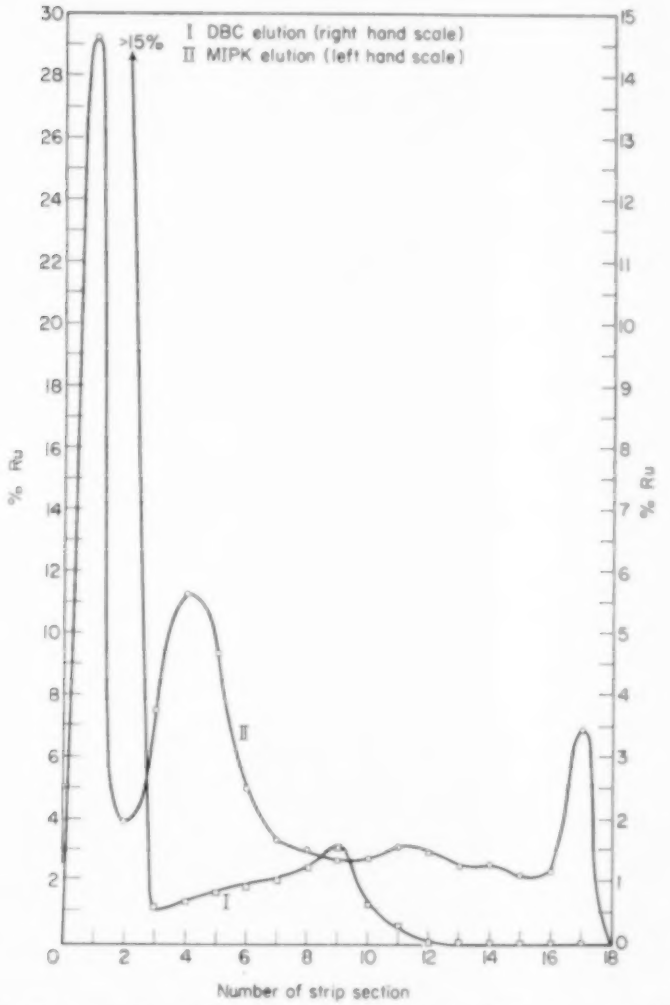



FIG. 2.—Chromatograms for RuNO nitrato complexes at equilibrium in 3 M $HNO_3$. $\sim 10^{-3}$ M Ru. Volume applied 1 $\mu$l.

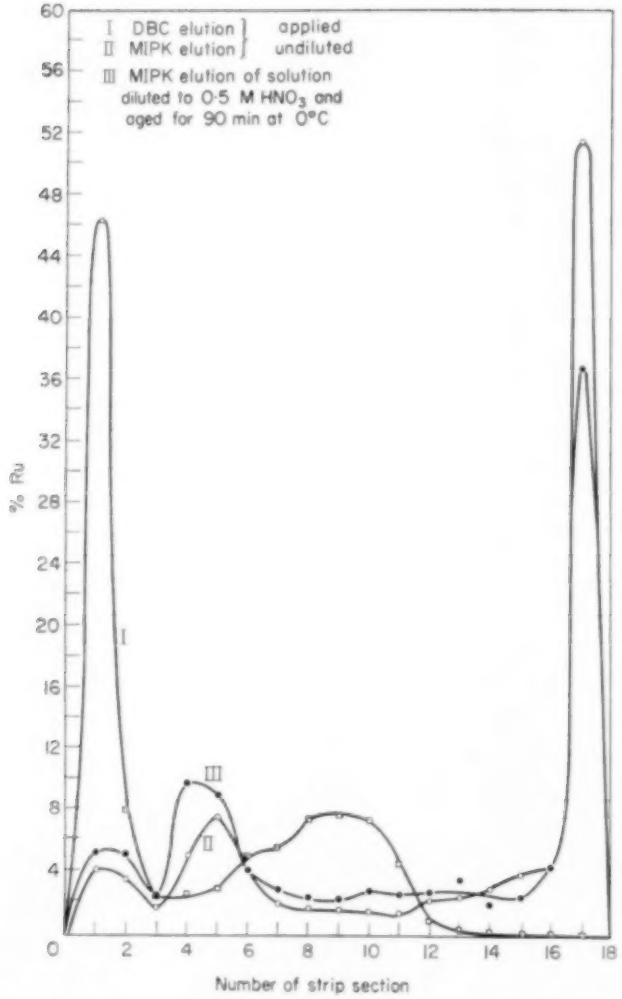

I DBC elution } applied
II MIPK elution } undiluted
III MIPK elution of solution diluted to 0·5 M $HNO_3$ and aged for 90 min at 0°C
% Ru
Number of strip section
I
II
III

FIG. 3.—Chromatograms for RuNO nitrato complexes at equilibrium in 7·8 M $HNO_3$. $5 \times 10^{-3}$ M Ru. Volume applied 5 $\mu$l.

Vol. 12 1959/60

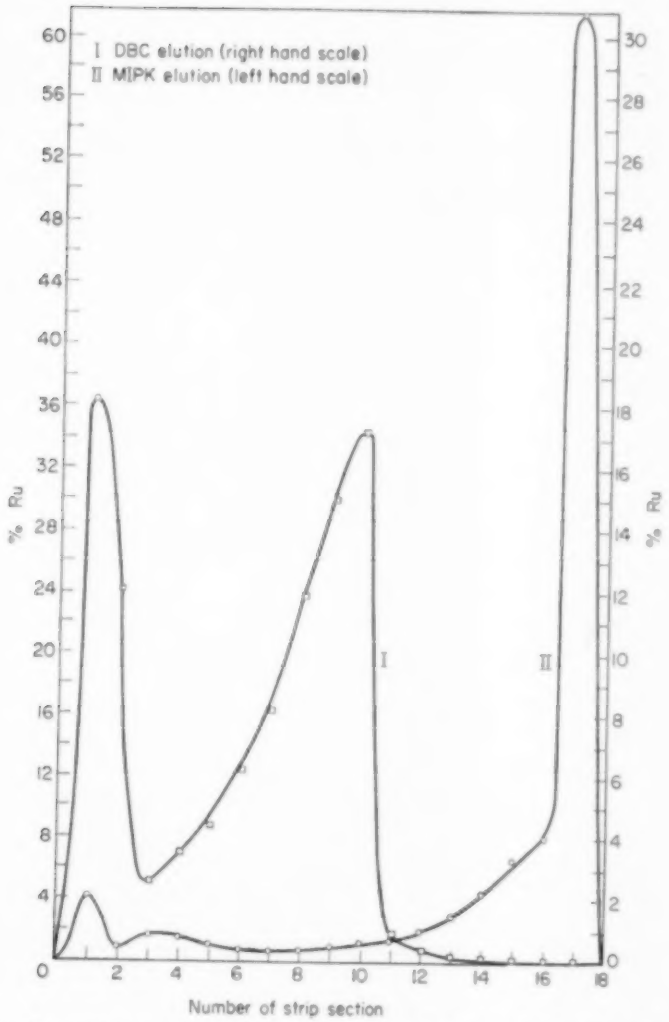



FIG. 4.—Chromatograms for RuNO nitrato complexes at equilibrium in 14·5 M $HNO_3$. $\sim 10^{-7}$ M Ru. Diluted to 3 M $HNO_3$ immediately prior to chromatography. Volume applied 1 $\mu$l.

## 2. SOLUTIONS AT EQUILIBRIUM IN NITRIC ACID

### (a) *Composition*

The mole fraction of complexes belonging to the four Groups (A, B, C, D) were determined for solutions at equilibrium in 0·1–15 M $HNO_3$, previously aged at room temperature (20 ± 1°) for at least 24 hr to ensure equilibrium. Results proved to be independent of the total ruthenium concentration, $C_{Ru}$, which ranged from $10^{-7}$ to $10^{-2}$ M : for instance, ruthenium distribution coefficients ($D_{Ru}$), after stirring solutions at equilibrium in 3 M $HNO_3$ for 30 sec at 0° with an equal volume of 30% TBP, were:

| $C_{Ru}$ | $3 \times 10^{-3}$ | $10^{-4}$ | $10^{-5}$ | $10^{-6}$ M |
|---|---|---|---|---|
| $D_{Ru}$ | 0·120 | 0·128 | 0·125, 0·128 | 0·120 |

(i) *By paper chromatography with dibutyl cellosolve elution* (Figs. 2, 3 and 4). The percentages of ruthenium on sections 3–13 (the peak has occurred on sections 8–10) after DBC elutions have been added together to give the mole percentage of ruthenium present as complexes of Group D (Table 3). Chromatograms in which the well-defined minimum usually found on section 3 was absent, e.g. because of the presence of excessive moisture, have been excluded. The proportion of ruthenium on sections 8–13 showed a relatively large increase with the nitric acid concentration (from 3·5% in 3M $HNO_3$ to 48% in 12–14M $HNO_3$) compared to the proportion on sections 3–7 (4% in 3M $HNO_3$ to 24% in 12–14M $HNO_3$). This observation, together with the shape of the chromatograms, has been held to indicate that more than one species is present on sections 3–13.

(ii) *By paper chromatography with methyl isopropyl ketone elution.* The chromatograms with MIPK elution (illustrated in Figs. 2, 3, 4 and 5) have been used to obtain the respective mole percentages of Groups A, B, C and D (Table 3). The chromatograms showed a minimum at section 3 (occasionally at section 2), a peak on sections 4 or 5 and no pronounced maximum between sections 7 and 16. Account has been taken of the backward spreading of the Group D complexes from section 17: this is particularly noticeable (Fig. 4) where this Group predominates, as for example in the more concentrated nitric acid solutions. (Similar behaviour occurs with MIPK elution of uranyl nitrate which also appears on the solvent front.) An allowance, amounting to about 10% of the value for Group D, has been made for this backward spreading. The ruthenium on certain intermediate sections (usually 3 and 7) has been divided between the groups which overlap on these sections. The ruthenium on sections 1, 2 and part of 3 has been attributed to Group A; part of that on 3, together with that on 4, 5, 6 and part of 7, to Group B; that on 17 with allowance for backward spreading on 15 and 16, to Group D; and the remainder, that on 7–16, to Group C.

The reproducibility of the method is exemplified by 10 chromatograms for various stock solutions in 3 M $HNO_3$ which have shown 31–38% of the ruthenium in Group A, 29–36% in Group B, 22–28% in Group C and 8–10% in Group D.

For other classes of compounds it has been found that there is a linear relationship between $\log(1/R_f - 1)$ and the number ($x$) of a particular group present in the molecule or complex: application of this rule gives:—

Vol. 12 1959/6

| Complexes | Assumed number of nitrato groups | $R_f$ value |
|---|---|---|
| Group | | |
| A | $x$ | 0·05 obs. |
| B | $x+1$ | 0·22 obs. |
| C | $x+2$ | 0·6 obs. |
| D | $x+3$ | 0·9 calc. |
| | $x+4$ | 0·98 calc. |

Abnormally high proportions of ruthenium have on occasion been found on section 1 due to the presence of RuIV polymer or of incompletely depolymerized nitrosylruthenium hydroxide.

(iii) *By solvent extraction (Kenny–Martin plots).* This method,[1,6] employed in the early stages of the present work, involved measuring the distribution coefficient of ruthenium under standard conditions; namely, stirring for 30 sec after pipetting small aliquots of the solutions under examination into a stirred mixture of nitric acid and

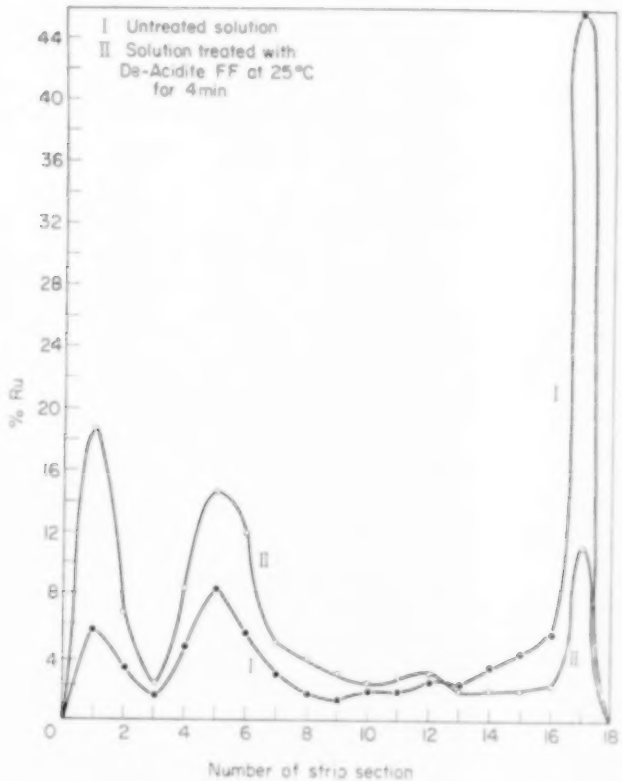



FIG. 5.—Chromatograms for RuNO nitrato complexes in 7·7 M $HNO_3$. $\sim 10^{-7}$ M Ru. Volume applied 1 $\mu$l MIPK elution.

[6] P. G. M. BROWN, J. M. FLETCHER and A. G. WAIN, AERE C/R 2260 (1957).

30% TBP at 0°, the nitric acid concentration being arranged so as to bring the final acidity to 3 M. From the distributions, the mole percentages of the more extractable species were calculated by established methods[6] and are included in Table 3. The calculations employed assume a single value for the partition coefficient of the complexes of Group D under the conditions of extraction, which is admittedly an approximation. Nevertheless the mole percentages of Group D found agree well with those from chromatography (Table 3); the divergence between the two methods for the mole percentages of Group C is not surprising since the boundaries of this Group are somewhat arbitrarily chosen.

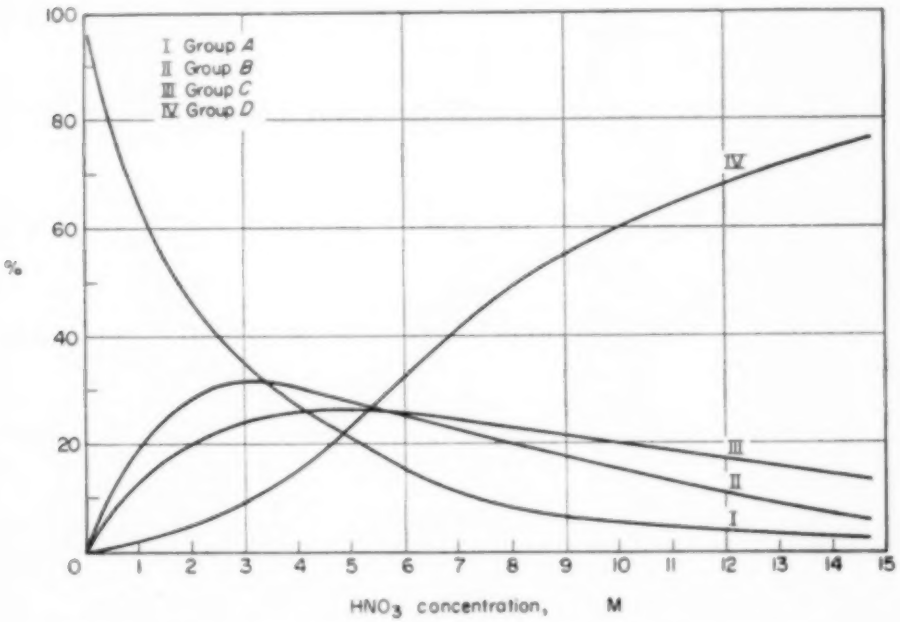



FIG. 6.—Relative mole fractions of Groups A, B, C, D of RuNO nitrato complexes at equilibrium in nitric acid solutions at ~20°C. ~$10^{-3}$ to $10^{-7}$ M Ru.

Smoothed curves derived from the results in Table 3 are shown in Fig. 6. In preparing these greater weight has been placed on the values obtained by chromatography than by solvent extraction. The curves in Fig. 6 are based on a large number of results obtained by the use of improved techniques, and are considered to represent the composition of solutions more accurately than the values given in earlier papers.[1,6]

The changes in the equilibrium composition with the nitric acid concentration (Fig. 6) which have been observed are primarily due, for reversible reactions of the type

$$[\text{Group B complex}]^{n} + NO_3^- \rightleftharpoons [\text{Group C complex}]^{n-1} + H_2O$$

Vol. 12 1959/6

to variation in the concentration of nitrate ions. That the position of equilibrium is independent of the hydrogen ion concentration is demonstrated by results obtained in nitric acid–nitrate mixtures:

| | Mole percentages as Group D complexes for total nitrate concentration of 5·5 M |
|---|---|
| In 5·5 M $HNO_3$ | 26% |
| In 3 M $HNO_3$ + uranyl nitrate | 27 |
| In 3 M $HNO_3$ + sodium nitrate | 20 |
| In 3 M $HNO_3$ + magnesium nitrate | 27 |

From the curves in Fig. 6, formation constants, K, can be calculated by the expressions (omitting certain activity coefficients):

$$\frac{\%\text{ as Group B}}{\%\text{ as Group A}} \cdot \frac{a_w}{C_{NO_3^-}}, \qquad \frac{\%\text{ as Group C}}{\%\text{ as Group B}} \cdot \frac{a_w}{C_{NO_3^-}}, \quad \text{etc.,}$$

where $a_w$ is the water activity and $C_{NO_3^-}$ the nitrate ion concentration. Values are given in Table 4 for the range 1–14 M $HNO_3$. HESFORD and MCKAY, in their analogous calculations of formation constants,[7] do not include the activity of water in their expressions. The omission makes little difference for solutions in dilute nitric

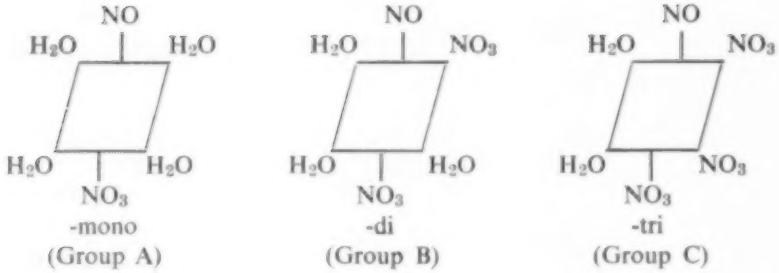
TABLE 4.—FORMATION CONSTANTS AT 20°C

| $HNO_3$ | $C_{NO_3^-}$ | $a_w$ | For complexes of Group B | C | D |
|---|---|---|---|---|---|
| 1 M | 0·99 | 0·97 | 0·29 | (0·67) | (0·19) |
| 3 | 2·75 | 0·88 | 0·29 | 0·24 | 0·12 |
| 4·5 | 3·75 | 0·79 | 0·25 | 0·19 | 0·16 |
| 7 | 4·9 | 0·62 | 0·28 | 0·14 | 0·22 |
| 10 | 5·1 | 0·44 | 0·24 | 0·12 | 0·26 |
| 12·5 | 4·4 | ~0·30 | (0·23) | 0·11 | 0·30 |

acid. Beyond 9 M $HNO_3$, however, without this factor a decrease in the mole percentage of Group D complexes would be expected because of the fall in the nitrate ion concentration (Fig. 3 of Ref. 7): in practice it is found that the mole percentage of Group D complexes continues to increase beyond 9M $HNO_3$ (Fig. 6). This increase in nitrato complexing at high nitric acid concentration, which is also found for other elements, e.g. Pu IV, indicates that the activity of water or the activity coefficients which have necessarily been omitted play an important role in this region.

The similarity in the values of the formation constants for Group B and Group C complexes suggests that the favoured configurations are

[7] E. HESFORD and H. A. C. MCKAY, *Trans. Faraday Soc.* **54**, 573 (1958).




since the second and third nitrato groups will both then be in positions *trans* to an aquo group. Because of the similarity of the remaining aquo group positions, it is to be expected that the values for $K_{tetra}$ and $K_{penta}$ would be approximately the same. If one assumes that the ratio of these formation constants is unity and that the Group D complexes are composed entirely of the pentanitrato and the 2-3-4-6 tetra-nitrato complexes, it can be calculated that the respective mole percentages of these are:

| $HNO_3$ | Mole percentages | | $K_{tetra}$ and $K_{penta}$ |
|---|---|---|---|
| | Tetra | Penta | |
| 3 M | 7% | 2% | 0·092 |
| 4·5 | 13 | 6·5 | 0·106 |
| 7 | 22 | 19·5 | 0·114 |
| 10 | 26 | 34 | 0·113 |
| 12·5 | 26 | 44 | 0·113 |

The formation constants on this basis for the di-, tri-, tetra-, and penta-nitrato complexes in, for example, 4·5 M $HNO_3$ at 20° are 0·25, 0·19, 0·11 and 0·11 respectively. Not only do these constants follow the trend of those of the nitrato complexes of $Th^{4+}$ and $Zr^{4+}$ but, for the latter, even the ratios $K_2/K_3$ and $K_3/K_4$ are very similar to those of $(RuNO)^{3+}$ (see below):

| | Medium | Ref. | $K_1$ | $K_2$ | $K_3$ | $K_4$ | $K_5$ | $K_1/K_2$ | $K_2/K_3$ | $K_3/K_4$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $(RuNO)^{3+}$ | 4·5 M $HNO_3$, 20° | above | — | 0·25 | 0·19 | 0·11 | 0·11 | — | 1·32 | 1·72 |
| $Th^{4+}$ | 2 M $HClO_4$, 20° | [8] | 6 | 2·1 | 0·78 | 0·55 | — | 2·86 | 2·70 | 1·41 |
| $Zr^{4+}$ | 4 M $HClO_4$, 20° | [9] | 2·18 | 0·59 | 0·43 | 0·28 | ~0·03 | 3·7 | 1·37 | 1·54 |

From these results it would be reasonable to infer a value of approximately 0·9 for $K_1$ for $RuNO^{3+}$. This implies that the contribution of the uncomplexed ions $[RuNO{\cdot}OH]^{2+}$ or $[RuNO]^{3+}$ to Group A is only significant in $<1$ M $HNO_3$.

The allocation of Group D complexes between tetra- and penta-nitrato complexes allows a better interpretation to be made of the chromatograms obtained with DBC elutions. The mole percentages calculated are consistent with a $R_f$ value of ~0·3 for

[8] V. V. FOMIN and E. P. MAIOROVA, *Zh. Neorg. Khim.* **1**, 1703, 2749 (1956).
[9] A. S. SOLOVKIN, *Zh. Neorg. Khim.* **2**, 611 (1957)

the tetranitrato complex and its appearance on sections 3–7, and a $R_f$ value of ~0·6 for the pentanitrato complex and its appearance on sections >8, with a peak on sections 9 or 10.

(b) *Evidence for charged complexes (treatment with ion exchange resins)*

Both anion and cation exchange resins remove ruthenium from solutions of these complexes in nitric acid (distribution coefficients as a function of the time of contact and of the nitric acid concentration are given in a later section). Experiments were conducted in 3 M $HNO_3$, i.e. under conditions such that the rapid proton dissociation from aquo groups, which occurs in very dilute nitric acid,[10] would be almost completely repressed. To ascertain the charge on the complexes of groups A, B, C and D, stock solutions were equilibrated with resins for times sufficiently short (3–4 min) to avoid appreciable reproportionation of complexes between the groups as a

TABLE 5.—COMPOSITION OF SOLUTIONS AFTER TREATMENT IN 3 M NITRIC ACID WITH ION EXCHANGE RESINS

| Nitric acid conc. of stock soln. | Resin treatment | % Ru not removed | Percentages as complexes of Groups | | | |
|---|---|---|---|---|---|---|
| | | | A | B | C | D‡ |
| 7·8 M | Nil | | 9 | 21 | 21 | 49, 47 |
| | Anion* | 33 | 25 | 38 | 26 | 11, 8 |
| | Anion† | 22 | 26 | 43 | 27 | 5, 10 |
| | Cation† | 55 | 7 | 22 | 30 | 41, 42 |
| 4·5 M | Nil | | 30 | 27 | 25 | 18, 20 |
| | Anion† | 40 | 41 | 33 | 17 | 9, 5 |
| | Cation† | 48 | 25 | 21 | 29 | 25, 21 |

* Equilibrated for 3 min at 0°C with 2·8 ml of solution per g resin.
† Equilibrated for 4 min at 25°C with 3·8 ml of solution per g resin.
‡ The first of each of the two values was obtained from the same MIPK elution as provided results for Groups A, B and C: the second was from a separate DBC elution.

result of the removal of particular complexes. The solutions were rapidly diluted to a nitric acid concentration of 3 M immediately before the experiments, and the equilibrations were carried out with relatively large volume ratios of resin to solution. The diluted solutions were analysed, both after equilibration with the resin and after standing the same length of time with no resin, by paper chromatography with MIPK and with DBC elutions.

The chromatograms (Table 5) showed that 90–95% of the complexes of Group D were removed by DeAcidite-FF; and that for the others, the amount removed decreased in the order Group C (60%)> Group B (40%)> Group A (<10%). (Fig. 5.)

The uptake of ruthenium by ZeoKarb 225, under the corresponding conditions, was appreciably less than for DeAcidite-FF. With the cation exchange resin the percentage removed (Table 5) decreased in the order Group A > Group B > Group C > Group D, i.e. in the reverse order to that found with the anion exchange resin.

From this evidence ion exchange between ZeoKarb 225 and Group D complexes and between DeAcidite-FF and Group A complexes would not be expected; nevertheless calculations based on Table 5 show that some removal does occur. This is

[10] I. L. JENKINS and A. G. WAIN, *J. Inorg. Nucl. Chem.* **3**, 28 (1956).

attributed to physical adsorption which becomes significant because of the high volume ratio of resin to solution.

Attempts to confirm the existence of anionic complexes by ion migration in aqueous solutions of 7–15 M $HNO_3$ were unsuccessful as the migration of ruthenium was very small. However, earlier ion migration experiments[11] on solutions made by dissolving a solid form of these nitrato complexes in acetone, diethyl ether and certain esters, showed the presence of anionic complexes.

(c) *Solvent extraction*

The manner in which we have defined the Group D complexes, i.e. by their $R_f$ value, implies that these are extracted preferentially to those of Groups A, B and C by a typical ketone (MIPK) and ether (DBC). Paper chromatography with TBP as the eluting solvent is difficult, because of its viscosity : however, ruthenium distribution measurements carried out under similar extraction conditions (from 3 M $HNO_3$ at 0°, by stirring equal volumes of the aqueous phase with 30% TBP for 30 sec) show that Group D complexes are also extracted preferentially by this solvent. Results for stock solutions diluted immediately prior to extraction, are:

| $HNO_3$ conc. of stock solution | 3 | 4·6 | 6·4 | 7·5 | 8·7 | 12·4 | 14·5 M |
|---|---|---|---|---|---|---|---|
| Ru as Group D complexes (from Fig. 6) | 9 | 20 | 36 | 45 | 53 | 70 | 76% |
| Ru found, after extraction, in org. phase | 9·1 | 20·1 | 34·6 | 41 | 48·5 | 66 | 72% |

The partition coefficients for Group D complexes must be $> 1$, and those for Group A, B and C complexes $< 1$, under these extraction conditions to account for these results.

It has been suggested[11] from earlier experiments using relatively short times of stirring (5 min) that the absence of enhanced solvent extraction in the presence of quaternary ammonium salts implies the absence of anionic complexes. We have extended the stirring times and found a small but significant increase in the ruthenium distribution coefficients when either a quaternary ammonium salt or a tertiary amine is present:

| Extraction from 3 M $HNO_3$ solutions by dibutyl carbitol | | | |
|---|---|---|---|
| Organic phase | $D_{Ru}$ for stirring time | | |
| | 5 min | 120 min | 240 min |
| Carbitol alone | 0·131 | 0·455 | 0·63 |
| Carbitol + 0·1 M tetraethyl ammonium nitrate | 0·135 | 0·492 | 0·685 |
| Carbitol + 0·1 M tri-n-octylamine | 0·151 | — | — |

[11] F. S. MARTIN and G. M. GILLIES, AERE C/R 973 (1952).

Vol. 12 1959/6

These results are interpreted to mean that organic solvents such as dibutyl carbitol themselves readily extract the tetranitrato and pentanitrato acids, for instance $H_2[RuNO(NO_3)_5]$, and that the enhanced extraction, which is very marked with uranyl nitrate, is accordingly relatively small in this case.

(d) *Absorption spectra*

The absorption spectra at $20 \pm 1°$ of mixtures of these nitrato complexes at equilibrium in various aqueous nitric acid concentrations are shown in Fig. 1. A Unicam SP 500 spectrophotometer with fused silica cells was used. As the degree of nitrato complexing increased, there was increased absorption, in particular from 390 m$\mu$ to 520 m$\mu$, together with the development of a broad band centred at 480 m$\mu$. At any particular acidity, Beer's law was obeyed.

## 3. DISTURBANCE OF EQUILIBRIA IN AQUEOUS NITRIC ACID

Because of the slow rates at which the nitrato complexes are converted into one another, relatively long times are required to re-establish equilibrium after it has been disturbed.

(a) *Dependence of rates of reaction on nitric acid concentration*

Stock solutions in 7·8, 11·1 and 12·2 M $HNO_3$ were diluted to either 0·5 M or to 3 M $HNO_3$ and aged at 0° or 25°. Chromatograms (DBC elution) of samples removed during the first hour of ageing in 3 M $HNO_3$ at 0° were almost identical, the mole fraction of Group D complexes being within $\pm 2\%$. Other results are given in Fig. 7. The rate constants ($k$) for the disappearance of Group D complexes, which are first order with respect to ruthenium, are:

| Medium | Temp. (°C) | $k$ (min$^{-1}$) | Half time (min) |
|---|---|---|---|
| 3 M $HNO_3$ | 0 | 0·0013 | 550 |
| 3 M $HNO_3$ | 25 | 0·024 | 30 |
| 0·5 M $HNO_3$ | 0 | 0·0024 | 300 |

Values nearly independent of the nitric acid concentration are to be expected for the aquation reactions causing the disappearance of Group D complexes:

$$[RuNO(NO_3)_4H_2O]^- + H_2O \longrightarrow [RuNO(NO_3)_3(H_2O)_2] + NO_3^-$$

$$[RuNO(NO_3)_5]^{2-} + 2H_2O \longrightarrow [RuNO(NO_3)_3(H_2O)_2] + 2NO_3^-$$

The temperature dependence indicates an energy of activation of ~ 19,000 cal with a frequency factor of ~ $10^{13}$.

The rate constant, 0·024 min$^{-1}$, found in 3 M $HNO_3$ at 25° may be considered in relation to the value (0·04 min$^{-1}$) taken from Table 4 in the paper by JENKINS and WAIN[10] for similar conditions. One of the methods which they employed (ruthenium distribution measurements after dilution of a stock solution in 7 M $HNO_3$) will have determined the rate of disappearance of Group D complexes (rather than the trinitrato complex only as they believed at the time). They commented that the energy of activation derived from their results, 6000 cal, was abnormally low. On the other hand, our value and its associated frequency factor are typical of this type of reaction

and indicate that the earlier results, some of which were obtained by dissolution of the solid and some by dilution of a stock solution, are probably unreliable.

The chromatography with MIPK elution of solutions of the complexes which had been aged after their nitric acid concentration had been increased from 1 to 7·5 M showed no pronounced preferential growth of a particular group of complexes. It is concluded from the curves in Fig. 5 that Groups A and B grow at approximately similar rates. The rate constants, which are first order with respect to ruthenium, for the reactions.

$$\text{Group A} \rightleftharpoons \text{Group B} \rightleftharpoons \text{Group C} \rightleftharpoons \text{Group D}$$

have therefore similar values for a particular direction.

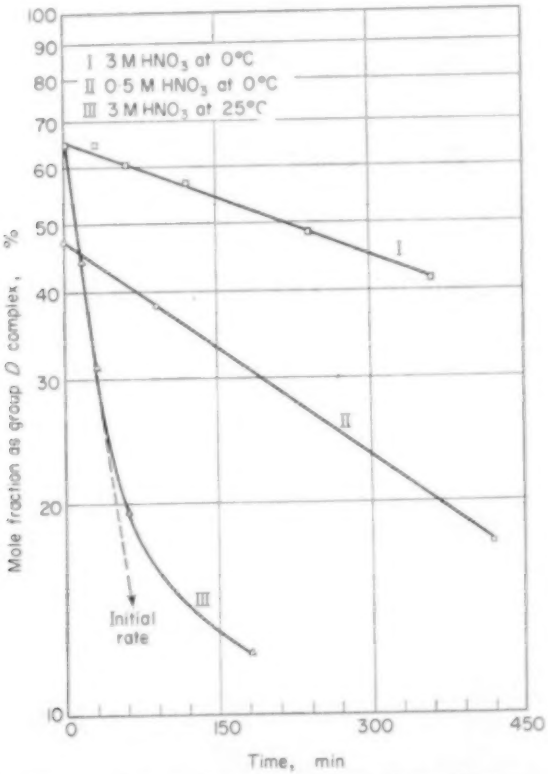



FIG. 7.—Rates of denitration of Group D complexes.

In the course of an hour the spectrophotometric absorption curve (cf. Fig. 1) of solutions diluted from 9 M to 1 M $HNO_3$ changed gradually over the whole range of wavelengths examined (330–580 m$\mu$). The absorption spectra of the various complexes are too similar to allow the rates of any of the reactions to be deduced.

(b) *Adsorption on anion exchange resin*

Portions of wet resin (1·5–3·5 ml) were stirred at 25° with 20 ml of solution. The amount of ruthenium removed increased considerably with time up to 30 min

Vol. 12 1959/6

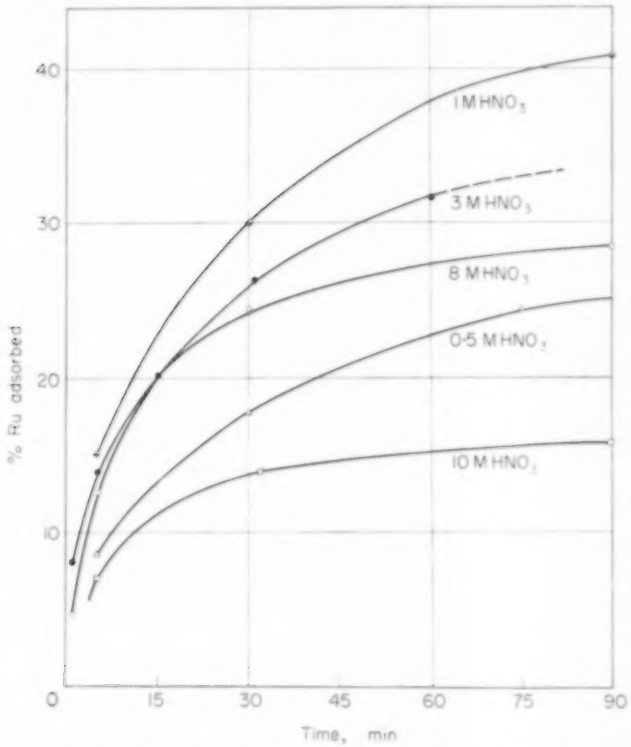



FIG. 8.—Rates of adsorption on deacidite-FF at 25°C of RuNO nitrato complexes aged to equilibrium in nitric acid solutions. $\sim 10^{-7}$ M Ru.

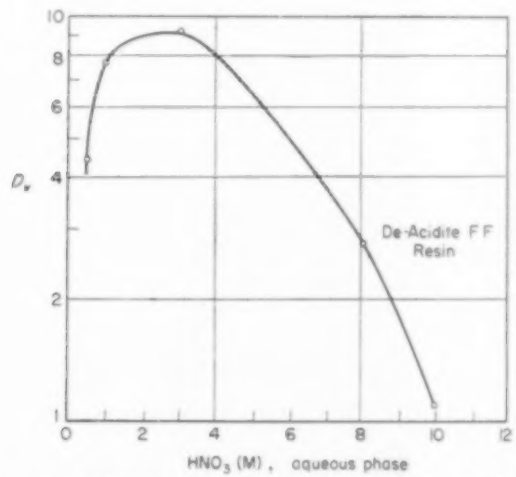



FIG. 9.—The variation of the ruthenium distribution coefficient at 25°C with nitric acid concentration for adsorption by an anion exchange resin.

(Fig. 8) and for a solution in 8 M $HNO_3$ became constant after 90 min, but required a rather longer time for solutions in less concentrated nitric acid. The relatively long times required for equilibrium to be reached are caused by the relatively slow rates of the nitration reactions by which those complexes withdrawn from solution are replenished.

The ruthenium distribution coefficient at equilibrium, $D_V$, is given by:

$$D_V = \frac{\text{activity adsorbed/ml resin}}{\text{activity remaining/ml solution}} = \frac{\%\text{ adsorbed}}{\%\text{ unadsorbed}} \times \frac{\text{vol. soln.}}{\text{vol. resin}}$$

The volume of the wet resin was measured to $\pm 5\%$ and the volume of interstitial acid calculated from the densities of the wet and dry resin. Values of $D_V$ are plotted in Fig. 9, and are independent of the ruthenium concentration within the range $10^{-3}$ to $10^{-7}$ M and also of the volume ratio of resin to solution. The curve passes through a maximum and its shape is similar to that found for many transition metals in acid solution.[12]

(c) *Solvent extraction*

The times required to reach equilibrium in solvent extraction are comparable to those required to reach equilibrium for adsorption by anion exchange resins. Thus, from a solution of these complexes which had been allowed to reach equilibrium in 3 M $HNO_3$,

(i) extraction by an equal volume of 30% TBP at 20° gave:

| Time | 0·5 | 10 | 30 | 60 | 180 | 660 min |
|---|---|---|---|---|---|---|
| $D_{Ru}$ | 0·074 | 0·093 | 0·119 | 0·146 | 0·167 | 0·167 |

and (ii) extraction by an equal volume of dibutyl carbitol at 20° gave:

| Time | 5 | 120 | 240 min |
|---|---|---|---|
| Ru in organic phase | 11·5 | 31 | 38·5% |

The ruthenium distribution coefficients obtained by SANGSTER[13] by stirring with 20% TBP at 20° until equilibrium was attained, were:

| $HNO_3$ | 0·75 | 1·5 | 2·2 | 2·9 | 3·6 M |
|---|---|---|---|---|---|
| $D_{Ru}$ | 0·30 | 0·23 | 0·14 | 0·08 | 0·065 |

The shape of the curve relating these results is dissimilar to those for the other metal nitrates that have been examined (Fig. 2 of Ref. 7) in that it falls rather than rises. Any maximum occurs at $< 0{\cdot}75$ M $HNO_3$ rather than in the range 4–6 M $HNO_3$ found for other nitrates.

[12] K. A. KRAUS and F. NELSON, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 113. United Nations, New York (1956).
[13] D. SANGSTER, AERE C/R 1533 (1954).

Vol. 12 1959/6

## DISCUSSION

The evidence provided by this work amplifies earlier results obtained with solutions of these complexes and completes the analogy between them and the chloro complexes, among which the anion $[RuNOCl_5]^{2-}$ is well known. On account of the inert nature of the nitrato complexes, quantitative information concerning both equilibria and kinetics had to be obtained by methods which are inapplicable to labile ones.

Our inferences are of interest in relation to the detailed consideration by HESFORD and MCKAY of the extraction of nitrato complexes from aqueous solutions by TBP.[9] For several metals this concerns species such as $[UO_2(NO_3)_2]$ which are uncharged in aqueous solution: it involves direct co-ordination of a molecule of TBP to the metal atom as in $[UO_2(NO_3)_2(TBP)_2]$. Extraction by TBP of acids, for instance $H[UO_2(NO_3)_3]$, which can be formed by enhanced nitrato complexing, is by comparison of negligible importance for many metals, although it can be highly significant in extraction by ethers and ketones.

The extraction by TBP of the nitrato complexes of nitrosylruthenium provides the first exception to this general behaviour. It is the Group D complexes, which we now recognise as consisting of the acids $H[RuNO(NO_3)_4]$ and $H_2[RuNO(NO_3)_5]$ in an unionised or ionised form, that are extracted by TBP in preference to the uncharged complex $[RuNO(NO_3)_3]$. The extraction of these acids depends on the co-ordination of TBP to hydrogen atoms in the undissociated acids, which is to say that it employs the same mechanism as that which determines the extraction by TBP of nitric acid itself. Because this mechanism demands no ligand substitution on the ruthenium atoms the instantaneous nature of the extraction of these inert complexes is understandable; and so also is the reason why the shape of the curve relating the distribution coefficients of metals (for TBP extraction) to the nitric acid concentration is different in the case of nitrosylruthenium from the general pattern shown by other metals.

*Acknowledgements*—We are grateful to Mr. B. F. GREENFIELD and Mr. S. A. J. PRATT for experimental assistance, to Mr. R. P. BELL, Dr. I. L. JENKINS, Dr. F. S. MARTIN and Mr. H. A. C. MCKAY for helpful discussions, and to Mr. W. P. GRIFFITHS for providing us with a sample of cobaltic cyclopentadiene.

Vol. 12 9/60

J. Inorg. Nucl. Chem., 1959, Vol. 12. pp. 174 to 180. Pergamon Press Ltd. Printed in Great Britain.

# THE INFLUENCE OF DILUENT POLARITY ON EXTRACTION OF PLUTONIUM COMPLEXES TO ORGANIC MEDIA

M. TAUBE

Department of Radiochemistry, Institute of Nuclear Research, Warsaw-Zeran

(*Received* 14 *January* 1959; *in revised form* 9 *April* 1959)

**Abstract**—The influence of the polarity of diluents on the extraction of plutonium (IV) complexes from nitric acid solution with tri-n-butylphosphate, di-n-butylphosphate, thenoyltrifluoroacetone, tetra-n-butylammoniumnitrate and methylisobutylketone has been examined. Diluents such as carbon tetrachloride, chloroform, benzene, cyclohexane, n-heptane, bromoform and dibromoethane have been used singly and in mixtures. Evidence is presented for the importance of the dipole moment of the diluent in the extraction process in connection both with the structure of the organic phase and dipole-dipole interaction promoting solvation of the Pu–complex. Maxima exist in the extraction of Pu–TBAN complexes to phases containing mixtures of polar diluents with non-polar diluents and in particular with benzene.

Vol.
12
1959/6

PREVIOUS workers[1–3] have drawn attention to the importance of the dipole moment and dielectric constant of the organic phase in connexion with extraction of metal complexes. The aim of the present work was to examine the influence of the polarity of diluents in organic phase on the extraction of tetravalent plutonium from a nitric acid aqueous phase. By diluent is here understood an organic substance of relatively simple structure, which itself is incapable of extracting plutonium to any significant extent.

## EXPERIMENTAL METHODS

As polar diluent chloroform was used, or in some cases, bromoform or dibromoethane, Benzene, carbon tetrachloride and in some cases cyclohexane and n-heptane were used as non-polar diluents. Using these diluents a study was made of the extraction of the relatively well known complexes of plutonium (IV) with the following agents: methylisobutylketone, (Hexone) tri-n-butylphosphate (TBP) di-n-butyl phosphate (DBP) thenoyltrifluoroacetone (TTA) tetra-n-butylammonium nitrate (TBAN). Use of these agents permitted study of the influences of diluent polarity on complexes of different types.

Organic solvents and complexing agents were purified by appropriate methods, with the exception of TTA. All other reagents were analytical grade. Plutonium (IV) nitrate was prepared in this laboratory by dissolution of high-purity plutonium metal.

Batch extractions were done with 1 ml organic and 1 ml aqueous phase, at room temperature, with 10 min shaking of phases in all cases, except TTA, for which the shaking time was 30 min. Aqueous phases were $5 \times 10^{-6}$ M in Pu prior to the extraction. Extraction was done in small cylindrical glass vessels, and phases separated by pipetting after standing for at least 30 min. Radiometric estimation of Pu was done with an $\alpha$-scintillation counter after evaporation of 20 $\mu$l aliquots on glass supports.

[1] A. G. GOBLE and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* **7**, 94 (1958).
[2] G. H. MORRISON and H. FREISER, *Solvent Extraction in Analytical Chemistry*, John Wiley, New York (1957).
[3] M. TAUBE, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, P/1587.

## RESULTS

Results of extraction in various systems are shown in Figs. 1–7. The following type of experimental system was used: a three-component organic phase in which the organic phase contains a constant proportion of the complexing agent, and two diluents present in various proportions.

## DISCUSSION

The extraction of plutonium by hexone falls rapidly with dilution of the complexing agent. From Fig. 1 it can be seen that the extraction of plutonium by hexone does not show any significant differences with regard to the diluting agents: chloroform, carbon tetrachloride and benzene. This insensibility to type of diluent

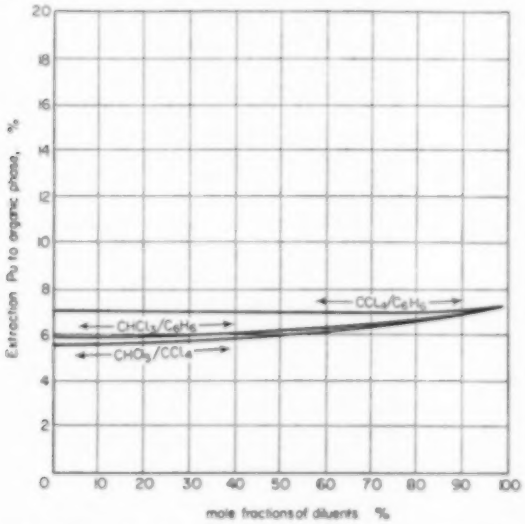



FIG. 1.—Plutonium extraction from 6 M $HNO_3$ to a three component organic phase.
Hexone + two diluents
Hexone mole fraction: 0·39–0·43.

was also confirmed for the following mixtures: cyclohexane/benzene, cyclohexane/chloroform and bromoform/benzene. It can be seen that extraction is not influenced by the polarity of the diluent mixture, although the relatively high proportion of hexone in the organic phase (0·4 mole fraction), restricts the significance of the result and prevents full comparison with the other systems studied here.

From Figs. 2 to 4, it can be seen that in the case of TBP, DBP and TTA the influence of the diluent in the organic phase is very similar. Extraction of plutonium to an organic phase diluted with either the non-polar carbon tetrachloride or benzene is almost identical, and is significantly greater than when polar chloroform is used as diluent. This greater extractability with non-polar diluents was also confirmed for the non-polar diluents: cyclohexane for TBP, and DBP; n-heptane for TBP, and the polar diluent, bromoform, for TBP, dibromomethane for TBP, DBP, TTA, in results not shown here. These additional experiments also confirmed that the extraction for a given complexing agent was identical when different non-polar diluents

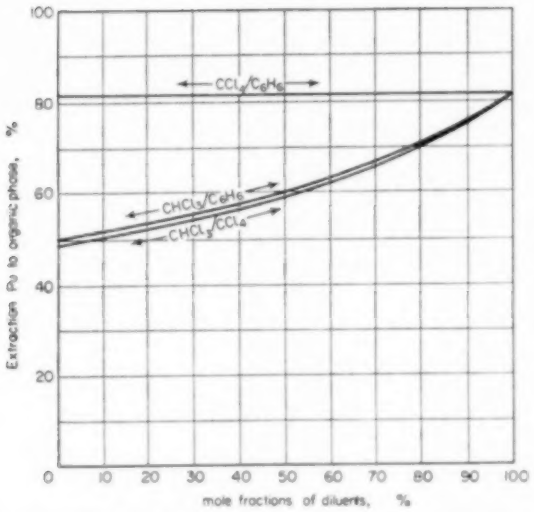



FIG. 2.—Plutonium extraction from 6 M $HNO_3$ to a three component organic phase.
TBP + two diluents
TBP mole fractions: 0·028

Vol. 12 1959/6

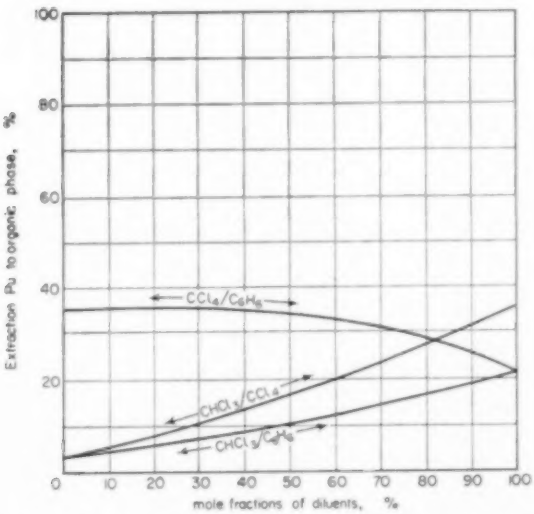



FIG. 3.—Plutonium extraction from 6 M $HNO_3$ to a three component organic phase.
DBP + two diluents
DBP mole fractions: $5 \times 10^{-4}$.

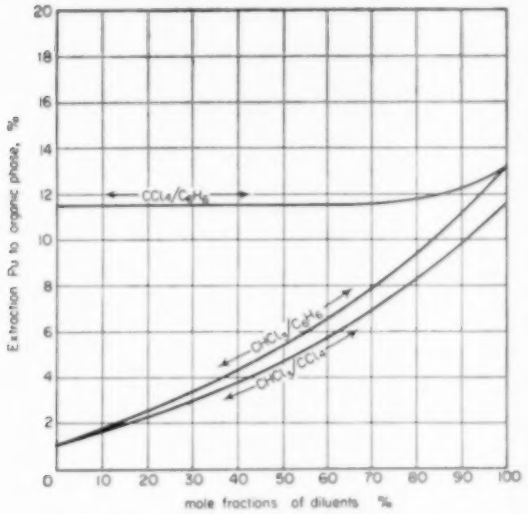



FIG. 4.—Plutonium extraction from 1 M $HNO_3$ to a three component organic phase.
TTA + two diluents
TTA mole fractions $4 \times 10^{-3}$.

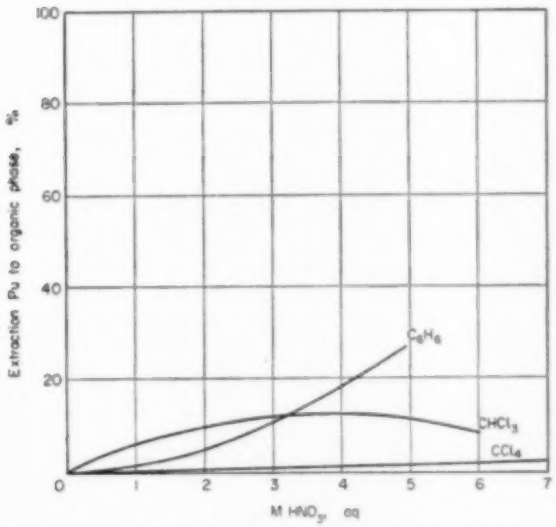



FIG. 5.—Plutonium extraction with TBAN as a function of $HNO_3$ concentration for three different pure diluents
TBAN mole fractions $2{\cdot}7 \times 10^{-4}$

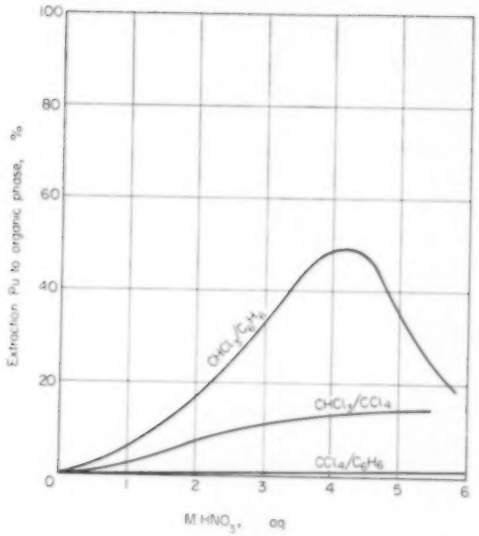



FIG. 6.—Plutonium extraction with TBAN as a function of $HNO_3$ concentration for three different mixed diluents
TBAN mole fractions $2{\cdot}7 \times 10^{-4}$
$CHCl_3/C_6H_6$ mixture (0·53 mole fractions $CHCl_3$)
$CHCl_3/CCl_4$ mixture (0·55 mole fractions $CHCl_3$)
$CCl_4/C_6H_6$ mixture (0·52 mole fractions $C_6H_6$)

Vol. 12 1959/6

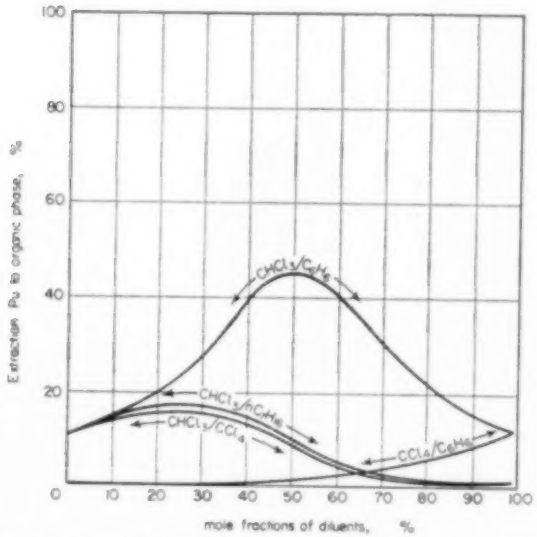



FIG. 7.—Plutonium extraction from 3 M $HNO_3$ to a three component organic phase: TBAN + two diluents
TBAN mole fractions $2{\cdot}7 \times 10^{-4}$.

were used, and that the percentage extraction for a given complexing agent was invariant when various mixtures of non-polar diluents were used.

From Figs. 5 to 7 it can be seen that extraction of the Pu–TBAN compound to a three-component phase shows the following characteristics. With progressive increase in mole fraction of carbon tetrachloride when a $CCl_4/CHCl_3$ mixture is used there is a slight rise in extraction followed by a marked decline. In the case of a $C_6H_6/CCl_4$ mixture there is a monotonic decline of extraction with increase in carbon tetrachloride mole fraction (Fig. 7). When a $C_6H_6/CHCl_3$ mixture is used, increase in mole fraction of chloroform is accompanied by rise of extraction to a very marked maximum, followed by a decline. In the case of the systems showing a maximum care was taken to check that the maximum was not due to changes of phase volume resulting from contacting aqueous solutions of nitric acid with the given phase. The maximum of extraction for the $CHCl_3/CCl_4$ mixture ($2{\cdot}7 \times 10^{-3}$ M TBAN; 3 M $HNO_3$) occurs at 0·25 mole fraction chloroform and is 1·2 times higher than for pure chloroform. The maximum of extraction for the $CHCl_3/C_6H_6$ mixture occurs at 0·50 mole fraction chloroform and is 3·5 times higher than for pure chloroform.

*A priori* it might be expected that amongst others the following factors would have an important influence on the extractability of plutonium in the systems studied here.

1. The interaction of the plutonium-complex dipole with permanent or induced diluent dipole.

2. The work necessary for hole formation in organic phase, dependent on the structure of the phase and in particular dipole moments of diluent molecules.

3. In the case of an ion pair, particularly Pu–TBAN, the degree of dissociation of the pair in organic phase, dependent in turn on dielectric constant of the diluent (1) and the dipole moment of the diluent molecules.

In connexion with the first and second of these it should be pointed out that plutonium complexes with TBP, DBP and TTA are probably symmetrical without significant dipole moment. Thus one would expect that dipole interaction with diluent would play no role, but that work concerned with hole formation would perhaps be significant for extraction, i.e. extraction* and somewhat greater than extraction with a polar diluent. The facts confirm this supposition.

With regard to the influence of the diluent on the degree of dissociation of complexes of the metal in the organic phase it might perhaps have been expected that dissociation of the Pu–TBAN complex yielding the metal in a complex anion, and thus increasing extraction, would be greater in chloroform than in benzene, since the former diluent has the greater dielectric constant.[1] As can be seen from Fig. 5 this is in fact the case for nitric acid molarities below 3 M. However in view of the additive property of dielectric constants in mixed solvents, on the basis solely of a dissociation mechanism one would expect a monotonic decline of extraction as benzene concentration is increased in mixture $C_6H_6/CHCl_3$ (Fig. 7). The existence of a marked maximum in this system shows that in this case a simple mechanism based only on dielectric constant and dissociation does not explain everything.

The existence of maxima for the extraction of Pu–TBAN in the mixture $CHCl_3/CCl_4$, $CHCl_3$/heptane, $CHCl_3$/cyclohexane and $CHCl_3/C_6H_6$ may possibly be explained as follows. As chloroform is progressively diluted with a non-polar

* To a non-polar medium would be marked.

diluent, the organic phase becomes less organized, and hole formation is thus facilitated, so that at first the percentage extraction increases. As dilution progresses further, however, the Pu–TBAN complex has less chance of solvation with polar chloroform and extraction thus declines.

The significantly greater extraction of Pu–TBAN to a phase of pure benzene diluent than to phase of pure carbon tetrachloride diluent (Fig. 5), n-heptene or cyclohexane, and also the significantly greater extraction maximum for mixture $C_6H_6/CHCl_3$ than for $CCl_4/CHCl_3$ n-heptane/$CHCl_3$ and cyclohexane/$CHCl_3$ requires separate treatment. An explanation might be that the relatively strong Pu–TBAN dipole can induce a dipole in benzene but not in carbon tetrachloride, n-heptane or cyclohexane, in view of greater polarizability of benzene, so that solvation in benzene is more extensive.

*Acknowledgements*—The author wishes to thank Prof. I. G. CAMPBELL and Dr. S. SIEKIERSKI for helpful discussions, Dr. A. SZUCHNIK for purification of some of the organic reagents, and Mr. W. KALINOWSKI for technical assistance.

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 181 to 185. Pergamon Press Ltd. Printed in Great Britain.

# A STUDY OF SOLUTIONS OF TITANIUM OF LOW OXIDATION STATES*

T. C. FRANKLIN and H. V. SEKLEMIAN†
Chemistry Department, Baylor University, Waco, Texas

(*Received* 17 *March* 1959)

**Abstract**—A study of a series of aqueous and non-aqueous solutions of titanium of low valence has shown that titanium exists in these solutions in the form of titanium (III). Polar titanium (II) chloride does not dissolve in the non-polar solvents studied. Solvents with active hydrogens react with the titanium (II) and in acetonitrile and dimethylformamide titanium (II) chloride undergoes disproportionation.

$$TiCl_2 \text{ (solid)} \rightarrow TiCl_3 \text{ (solution)} + Ti \text{ (solid)}$$

RECENTLY GUTMANN and NOWOTNY[1] reported on a study of non-aqueous solutions supposedly containing titanium (II). A similar but more extensive study on this phase of their work is reported here.

The problem was broken into two parts:

(1) A study of methods that might be thought to produce titanium (II) in solution; and
(2) A study of solutions made by mixing titanium (II) salts with various solvents.

## 1. METHODS OF SYNTHESIS OF TITANIUM (II)

Attempts were made to prepare titanium (II) in solution by:
(A) Reduction of titanium (IV) chloride with active metals
(B) Dissolution of titanium metal in acids
(C) Anodic dissolution of titanium in several non-aqueous solvents.

### A. *Reduction experiments*

Titanium (IV) chloride was dissolved in the solvent and refluxed under nitrogen in the presence of magnesium or aluminium for 2 hr. In most cases the reactions were so vigorous in the early stages that the vessels had to be cooled in an ice-bath. The solvents used were acetonitrile, dimethylformamide, nitrobenzene and acetic acid, dried over either potassium hydroxide or drierite.

The colours of the solutions were noted during the reduction; the solutions were tested for reaction with hydrochloric acid; and where possible the solutions were titrated with a solution of bromine in the solvent used. The end point was observed visually and potentiometrically using a Beckman model H pH meter. All experiments indicated that these reductions produced titanium (III) only.

### B. *Dissolution of titanium in acids*

A study was made of the dissolution of titanium in concentrated aqueous solutions of hydrochloric, sulphuric, hydrofluoric and a mixture of hydrochloric and acetic acids; and in acetic acid made anhydrous with acetyl chloride.

* This research was supported in whole or in part by the United States Air Force under Contract Nr. AF 33(616)-3331, monitored by Acro Research Laboratory.
† Present address Union Carbide Metals Co., Niagara Falls, New York.
[1] V. GUTMANN and H. NOWOTNY, *Monatsh. Chem.* **89**, 331 (1958).

*Aqueous acid solutions.* The valence of the titanium was checked both by volume of hydrogen evolved and by titration with ferric ammonium sulphate as the titrant and ammonium thiocyanate as the indicator.[2]

All experiments led to the conclusion that in these aqueous solutions the titanium dissolved with a valence of three in agreement with previously reported experiments.[3]

*Acetic acid.* Investigation of the anhydrous acetic acid solution was hindered by two things. It was impossible to measure the valence by the volume of hydrogen evolved since there was no measurable volume of gas evolved in the gas burette. In addition, since no reference was found to a completely anhydrous oxidation reduction titration for use in systems such as these it was necessary to develop a coulometric method for use.

The apparatus is pictured in Fig. 1. The coulometer was a semimicro oxy-hydrogen coulometer similar to that of LINGANE.[4] The current was held at approximately 3 mA. Since the titanium solutions were highly coloured, the sudden change of this colour to a light yellow was taken as the end point.

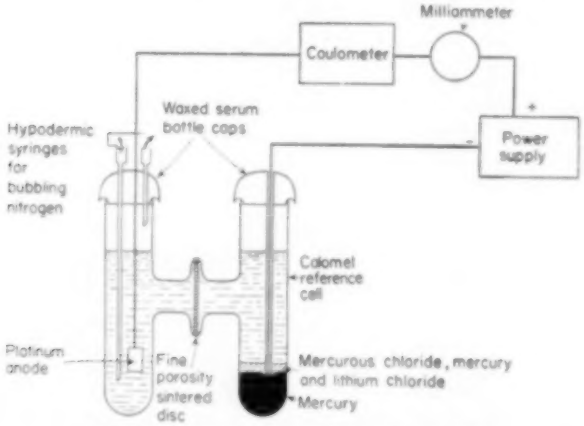



FIG. 1.—Apparatus for coulometric analysis.

The reference cell was a saturated calomel electrode with the solvent being acetic acid. The solution in the reference cell was saturated with either anhydrous lithium chloride or anhydrous tetramethylammonium chloride. To remove oxygen, the dry solvent in the anode compartment was bubbled with $N_2$, using hypodermic needles as both the inlet and outlet. After bubbling, the needles were removed. The serum bottle caps on top of the H tube were recoated with paraffin every time a needle was removed to prevent air leakage. A sample was withdrawn from the reaction vessel with a tuberculin syringe, inserted in the H cell, and titrated. This method of titration was checked using both lead tetroacetate and iodine.

The total titanium in the reaction vessel was determined colorimetrically using a Leitz colorimeter and the basic procedure given in BARKSDALE.[5]

The results for the anhydrous acetic acid solutions are shown in Table 1.

It will be noted that the valence lies between three and four. Later it was observed that a fine black powder (probably titanium) was left after the reaction was over and colorimetric analysis showed that the titanium in solution was less than the amount of titanium placed in the system. Therefore, the valences undoubtedly lie much closer to three.

C. *Anodic dissolution of titanium*

*Experimental.* A number of experiments studying the anodic dissolution of titanium were carried out using a stoppered porous cup for the anode compartment inserted in the open cathode

[2] J. BARKSDALE, *Titanium* p.112. Ronald Press, New York (1949).
[3] *Gmelin's Handbuch der Anorganischen Chemie*, System—Number 41, *Titan*, Verlag Chemie GMBH, Weinhem (1951).
[4] J. J. LINGANE, *J. Amer. Chem. Soc.* **67**, 1916 (1945).
[5] J. BARKSDALE, *Titanium*. Ronald Press, New York (1949).

Vol. 12 1959/60

compartment. The cathode was a strip of lead and the anode was titanium. The solvents used are listed in the table of results. The anodic oxidation was carried out under a dry, deoxygenated nitrogen atmosphere. A levelling bulb was connected to the anode compartment and the level inside the anode compartment was maintained constant by adding or removing solvent in order to keep the current density constant. Most runs were made at room temperature. However, in order to minimize electro-osmosis, a number of runs were made in a refrigerated box at 7·0°C.

TABLE 1

| Run No. | No. of titrations | Average valence of titanium in solution | Average deviation of the mean |
|---|---|---|---|
| 1 | 5 | 3·43 | ±0·10 |
| 2 | 5 | 3·34 | ±0·05 |

The current density ranged from 0·0005 to 0·02 A per in$^2$. The cathode compartment contained the solvent studied plus a small amount of titanium (IV) chloride to lower the resistance.

The coulometer was an oxy-hydrogen coulometer. The amount of titanium dissolved was determined by weighing the anode before and after the experiment.

As can be seen from Table 2, all valences lie between three and four. The addition of complexing agents, if it did anything, raised the valence of the titanium going into solution.

## RESULTS AND DISCUSSION OF RESULTS

Table 2 summarizes the results of the anodic dissolution experiments.

TABLE 2

| Solvent used | Drying agent | Number of runs | Number of faradays per mole of titanium dissolved | Average deviation of the mean |
|---|---|---|---|---|
| Dimethylformamide | Drierite | 9 | 3·56 | ±0·51 |
| Acetonitrile | Potassium hydroxide | 35 | 3·00 | ±0·29 |
| Formamide | Drierite | 4 | 3·72 | ±0·38 |
| Acetonitrile plus 8-hydroxyquinoline | Potassium hydroxide | 2 | 3·00 | ±0·16 |
| Acetonitrile plus pyridine | Potassium hydroxide | 1 | An apparent electrolyte reaction with the solvent | |
| Acetonitrile plus Diphenylthiocarbizone | Potassium hydroxide | 3 | 3·03 | ±0·10 |
| Acetonitrile plus α, α′ dipyridyl | Potassium hydroxide | 2 | 3·94 | ±0·76 |
| Dimethylformamide plus 8-hydroxy-quinoline | Drierite | 2 | 3·17 | ±0·03 |
| Dimethylformamide plus ammonium fluoride | Drierite | 1 | 3·60 | |

## 2. EXTRACTS OF TITANIUM (II) SALTS

Studies were made of the supernatant solution obtained by mixing solids known to contain titanium (II) with various solvents.

*Experimental.* Three sources of titanium (II) were used:

(a) Titanium (II) bromide obtained by vacuum disproportionation of titanium (III) bromide;[6]

(b) The fused salt melt used in the electroplating of titanium. The sample was obtained from Dr. T. A. Henrie of Electro Metallurgical Co. and was reported to have the following composition:

| | |
|---|---|
| Titanium (II) chloride | 36·5% |
| Titanium (III) chloride | 2·85% |
| Total titanium | 15·50% |
| Sodium chloride | 60·41% |
| Iron | 0·009%; |

(c) Titanium (II) chloride from the New Jersey Zinc Co.

*Experimental.* The solvents studied were the best grade commercially available, dried with either drierite or potassium hydroxide and deoxygenated by bubbling with dry, oxygen-free nitrogen. All operations were carried out in a dry box under a nitrogen atmosphere. The solid material was added to a test-tube containing the various solvents. They were then stoppered and coated with paraffin. After several days, samples were withdrawn with a hypodermic needle and added to dilute hydrochloric acid in a Warburg manometer and tested for the evolution of gas.

TABLE 3.—EXTRACTION OF TITANIUM (II) DICHLORIDE

| Solvent | Behaviour and appearance of solutions |
|---|---|
| Dioxane, benzene, dimethylaniline | No dissolution |
| Acetonitrile, dimethylformamide | Green at first—developed a blue layer on standing |
| γ-Butyrolactone | |
| Acetone, tetrahydrofuran | Green solution—yellow to orange top layer |
| Formamide* | Dark green solution |
| Pyridine* | Red to dark reddish-brown solution |
| Diethylamine* | Purplish precipitate formed |
| Pyridine* + *o*-phenanthroline | Blue to purple |
| Pyridine* + α, α′ dipyridyl | Blue to purple |
| Pyridine* + thiocarbizone | Blue to purple |

* In all formamide, diethylamine and pryidine solutions, gas bubbles were formed and a pressure was built up indicating the evolution of a gas from a reaction of the divalent chloride with the solvent.

The acetonitrile, dimethylformamide and pyridine solutions were examined spectrophotometrically with a Beckman DK-I spectrophotometer.

The acetonitrile solutions were examined polarographically using a dropping mercury electrode, a mercury pool as reference electrodes, tetramethylammonium chloride as a supporting electrolyte and a Sargent model XXI polarograph.

Coulometric analyses to determine the valence of titanium in solution were made on some of the acetonitrile, dimethylformamide and pyridine solutions. The procedure and equipment was essentially the same as that described in the dissolution section. The solvent studied was used as the solvent in both the reference electrode as well as the analysis compartment. In pyridine, however, it was necessary that the reference electrode be a copper, cupric chloride electrode. The total titanium content was determined colorimetrically as before (Table 3).

In no case was pressure built up in the Warburg apparatus when the solution was added to dilute hydrochloric acid, indicating that no reaction occurred between the solutions and the hydrochloric acid.

Comparison was made between the absorption spectra of titanium (IV) chloride, titanium (III) chloride and the absorption spectra of the acetonitrile, dimethylformamide and pyridine solutions. All solutions showed the presence of an absorption maximum around 300 mμ, probably due to the

[6] W. C. SCHUMB and R. F. SUNSTROM, *J. Amer. Soc.* **55**, 596 (1933).

Vol. 12 1959/60

titanium (IV) chloride. As reported by HARTMANN *et al.*,[7,8] titanium (III) has an absorption maximum around 480 mμ. All of these solutions absorbed in this region. No other absorption maximum was observed.

Polarographic studies of the acetonitrile extracts gave no waves other than those for the oxidation of titanium (III) and the reduction of titanium (IV).

The results from the coulometric analyses of the solutions are summarized in Table 4.

TABLE 4.—COULOMETRIC ANALYSIS OF EXTRACTS OF TITANIUM DICHLORIDE

| Solvent | Number of Runs | Valence of titanium in solution | Average deviation of the mean |
|---|---|---|---|
| Dimethylformamide | 3 | 2·96 | ±0·003 |
| Acetonitrile | 4 | 2·92 | ±0·042 |
| Pyridine | 3 | 3·86 | ±0·004 |

As was noted in Table 4, pyridine apparently undergoes some reaction with the titanium (II), which accounts for the high value of the valence found in the pyridine solution. In dimethylformamide and acetonitrile, the valence was found to be essentially three.

All of these experiments, including both the synthesis and the study of properties, lead to the conclusion that with these solvents, titanium (II) does not exist to any extent in solution.

It is reasonable to expect that the highly reactive titanium (II) would not exist in solutions containing solvents with active hydrogens such as acetic acid, water and formamide since it would react with these solvents. It is also reasonable to expect that titanium (II) would not exist in solutions in which the solvent was nonpolar such as benzene since the polar titanium (II) chloride would be insoluble. However, it was difficult to visualize why titanium (II) did not exist in dimethylformamide and acetonitrile solution. X-ray diffraction studies of the solid left after the titanium (II) chloride was shaken with these solvents showed the presence of titanium metal showing that the titanium (II) chloride had undergone disproportionation.

$$TiCl_2\,(\text{solid}) \rightleftharpoons TiCl_3\ (\text{solution}) + Ti\,(\text{solid})$$

This equilibrium is probably displaced to the right because of the high solubility of the titanium (III) chloride and the low solubility of titanium (II) chloride.

From this, it would appear that the experiments carried out by GUTMANN and NOWOTNY on solutions supposedly containing titanium (II) were, in reality, experiments on solutions of titanium (III).

[7] H. HARTMANN and H. L. SCHLÄFER, *Z. Phys. Chem.* **197**, 116 (1951).
[8] H. HARTMANN, H. L. SCHLÄFER and K. HANSEN *Z Anorg. Chem.* **284**, 153 (1956).

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 186 to 192. Pergamon Press Ltd. Printed in Great Britain.

# THE STABILITY OF AQUEOUS SOLUTIONS OF HYDROXYLAMINE-*O*-SULPHONIC ACID

H. J. MATSUGUMA* and L. F. AUDRIETH
University of Illinois, Urbana, Illinois

(*Received* 31 *March* 1959)

**Abstract**—Aqueous solutions of hydroxylamine-*O*-sulphonic acid, $H_2NOSO_3H$, undergo two principal modes of decomposition entailing (a) hydrolysis to hydroxylammonium ion and (b) self oxidation–reduction to give nitrogen and ammonia. The hydrolytic reaction is acid catalysed; disproportionation is markedly catalysed by presence of trace quantities of Cu(II) and is also favoured in alkaline solution.

THE chemical similarity between hydroxylamine-*O*-sulphonic acid (HOS) and chloramine was first noted by SOMMER[1]. Both substances are excellent aminating agents and both compounds undergo hydrolysis and decomposition to give nitrogen and ammonia. HOS is, however, the more stable of the two compounds since it can be prepared as a pure crystalline product by the sulphonation of hydroxylamine in 100% $H_2SO_4$ as solvent and can therefore be handled more easily than chloramine.

The powerful aminating action of HOS was first evaluated by SOMMER *et al.*[2] who effected the conversion of ammonia into hydrazine and showed that the conditions under which this process takes place are in many respects similar to those which characterize the Raschig synthesis from ammonia and chloramine. These same investigators also showed that typical primary, secondary and cyclic amines can be converted into the corresponding N-mono- and N-di-substituted hydrazines and that ethylenediamine gives 1-hydrazino-2-aminoethane. The behaviour of HOS as an ammonating agent was exploited subsequently by other investigators. BERGER[3] was able to prepare hydrazino-acids from amino acids by adding HOS to hot alkaline solutions of the latter. KELLER and SMITH [4,5] have used HOS to effect the amination of aromatic hydrocarbons in the presence of aluminium chloride as a catalyst. Oximes and amides have been obtained by heating ketone–HOS mixtures. GEVER and co-workers[6,7] have used HOS to prepare N-substituted hydrazines from the appropriate amines. MEUWSEN has effected the amination of tertiary amines to trialkylhydrazinium salts[8] and of imidodisulphonates to the hydrazino-1, 1, 2-trisulphonates[9]; APPEL[10] has employed HOS to effect amination of tertiary phosphines.

Vol. 12 1959/6

* Present address: Chemical Research Division, Picatinny Arsenal, Dover, N.J.

(1) F. SOMMER and H. G. TEMPLIN, *Ber. Dtsch. Chem. Ges*, **47**, 1221 (1914).
(2) F. SOMMER, O. F. SCHULZ and M. NASSAU, *Z. Anorg. Chem.* **147**, 142 (1925)
(3) H. BERGER, *Z. Prakt. Chem.* **152**, 270, 300 (1939).
(4) R. N. KELLER and P. A. S. SMITH, *J. Amer. Chem. Soc.* **66**, 1122 (1944).
(5) R. N. KELLER and P. A. S. SMITH, *J. Amer. Chem. Soc.* **68**, 899 (1946).
(6) G. GEVER and K. HAYES, *J. Org. Chem.* **14**, 813 (1949)
(7) G. GEVER, *J. Amer. Chem. Soc.* **76**, 1283 (1954).
(8) A. MEUWSEN and R. GÖSL, *Angew. Chem.* **69**, 754 (1957)
(9) A. MEUWSEN and H. TISCHER, *Z. Anorg. Chem.* **294**, 282 (1958).
(10) R. APPEL, W. BÜCHNER and E. GUTH, *Ann. Chem.* **618**, 53 (1958).

All these reactions may be regarded as displacement reactions, or from a more formalistic point of view as processes entailing amination (ammonation, nitridation) through the intermediate formation of a hypothetical imide molecule or radical. As imide donors HOS, $NH_2Cl$, $HN_3$ and even hydroxylamine and hydrazine can be represented by the empirical formula HNX (where X = $H_2SO_4$, HCl, $N_2$, $H_2O$ and $NH_3$ respectively). The HN molecule is isoelectronic with atomic oxygen; it can be regarded as the ammono analog of active oxygen. Each of these compounds can therefore be regarded as a nitridizing agent.

To further evaluate the usefulness of HOS as an aminating agent, we have undertaken to study the stability of aqueous solutions of HOS under various conditions. The results of a kinetic study on the hydrolysis of HOS in the temperature range 55–85° were reported briefly by HARNSBERGER and MORONEY[11] in 1952. No experimental details were given beyond the fact that hydrolysis was found to be first order when the pH is kept constant and that a minimum rate is observed at a pH of about 0·5. Two competing mechanisms were proposed to account for this behaviour; an uncatalysed reaction through the anion of the free acid and an acid catalysed reaction through the unionized acid. The acid ionization constant was found from kinetic data to be $1{\cdot}7 \times 10^{-2}$ in good agreement with the measured value. The activation energies and frequency factors for the two reactions were found to be significantly different. The rate of hydrolysis was found to depend linearly upon the ionic strength (in the range 0·1–1·0) of the solution. These authors also noted pronounced secondary salt effects when sulphate ion or the anion of an organic acid were substituted for the chloride ion used in most of the buffer solutions. SOMMER[2] had also pointed out that the stability of HOS is greatly reduced as the pH is raised and that decomposition takes place readily in alkaline solution to give nitrogen and ammonia. Traces of hydrazine and hydrogen azide were also found to have been formed during the decomposition of alkaline solutions of HOS.

The experimental work which is presented below encompasses a study of the stability of aqueous solutions of HOS in the acid range. Reactions of hydrolysis and of disproportionation take place concurrently. The disproportionation reaction representing a self-oxidation–reduction reaction to give ammonia and nitrogen in equimolecular quantities is markedly catalysed by the presence of trace quantities of dissolved copper.*

## EXPERIMENTAL

*Analytical.* Details for the preparation of HOS and for the iodometric procedure used in its analysis are published elsewhere.[12] The preparative method can be modified by addition of sulphur trioxide to a concentrated solution of hydroxylammonium sulphate in 95–98 per cent $H_2SO_4$. The HOS prepared by this procedure must be washed thoroughly with ether to remove adhering solvent and should be stored in a moisture-free atmosphere.

The iodometric procedure is based upon oxidation of iodide ion to free iodine by HOS, in acid solution. Presence of the hydroxylammonium ion and/or ammonium ion does not interfere. Neither the Raschig method[13] for determination of hydroxylamine nor the Kjeldahl procedure for ammonia can be used in the presence of HOS.

* Unpublished work by M. M. JONES in this laboratory has shown that trace amounts of copper greatly catalyse and accelerate the decomposition of chloramine.

[11] H. E. HARNSBERGER and J. P. MORONEY. Paper presented at the 121st meeting of the American Chemical Society, Buffalo, New York, March 1952.

[12] H. J. MATSUGUMA and L. F. AUDRIETH, *Inorganic Syntheses* Vol. V, p. 122. John Wiley, New York (1957).

[13] W. C. BRAY, M. E. SIMPSON and A. A. MACKENZIE, *J. Amer. Chem. Soc.* **41**, 1363 (1919).

HOS may be titrated quite readily with strong base. The pH curves obtained from such titrations (see Fig. 1) are typical of the titration of a strong acid, but show two distinct inflexion points. The major break occurs at a pH of 3·5–4·5, whereas a second break of small and of variable extent occurs over a pH range of 8–10. The second break is invariably smaller when cold solutions (0–2°C) are titrated. The second inflexion point is therefore considered to be due to hydroxylammonium ion, either as an impurity or as the product of hydrolysis as the pH of the solution rises during addition of standard base. Other curves in Fig. 1 show the titration of dihydroxylammonium sulphate (Curve 2) and of a mixture of the mono- and dihydroxylammonium sulphates (Curve 3) with standard base. In both cases, the hydroxylammonium ion is neutralized at a pH of 8–11, indicating that the second break in the HOS titration curve is indeed due to the presence of the hydroxylammonium ion. The latter can therefore be determined quantitatively in the presence of HOS by titration with sodium hydroxide.

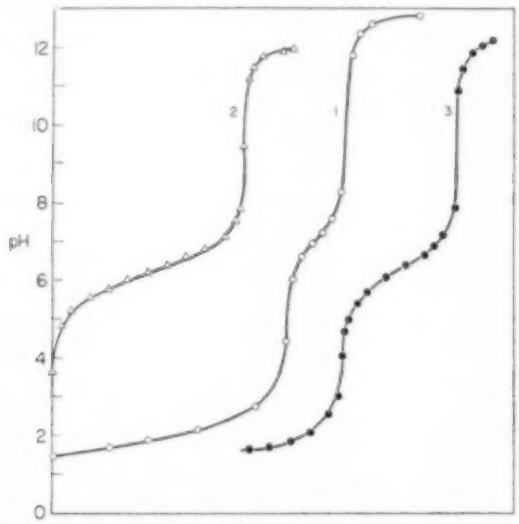



FIG. 1.—pH titration curves with NaOH as titrant: (1) HOS at 0–2°; (2) $(NH_2OH)_2 \cdot H_2SO_4$; (3) Mixture of $NH_2OH \cdot H_2SO_4$ and $(NH_2OH)_2 \cdot H_2SO_4$.

The decomposition of HOS in aqueous media was studied at three different temperatures [6·0–6·5, 23·35° and 100°C (reflux)] by pH titration, iodometric analysis, permanganometric analysis and by mass spectrometric analysis of gaseous decomposition products. The pH titrations were carried out at 0–2°C using a Beckman model G glass electrode pH meter, with sodium hydroxide as the titrant. The strong acid titer of HOS solutions was determined by titration to the bromcresol green endpoint (pH 3·5–4·5) and the total acid titer by titration to the phenolphthalein endpoint (pH 8–10). The iodometric procedure was used to determine the residual HOS content of solutions under study. For solutions in which complete decomposition of HOS had taken place the hydroxylammonium ion content was determined by the indirect permanganometric procedure.[13] Samples of gases for mass spectrometric analysis were collected from solutions of HOS by freezing out water vapour in cellosolve-dry ice traps. The solutions were degassed several times before the actual samples were taken at pressures of 5–10 $\mu$ Hg.

The effect of various additives such as sulphuric acid, added base, and copper(II) chloride upon the extent of decomposition of the HOS solutions was also evaluated. The initial HOS concentration was maintained at 0·1 M in all experiments; appropriate solutions also were made 0·12 N in added sulphuric acid and sodium hydroxide, respectively. The effect of copper(II) additive was determined in solutions 0·1 M in HOS and $10^{-4}$ M in added copper(II) chloride.

The data presented graphically in Fig. 2 represent the results obtained from a series of HOS solutions containing various additives and allowed to stand for the indicated times at 6·00–6·50°C. From these data it is evident that:

Vol. 12 1959/6

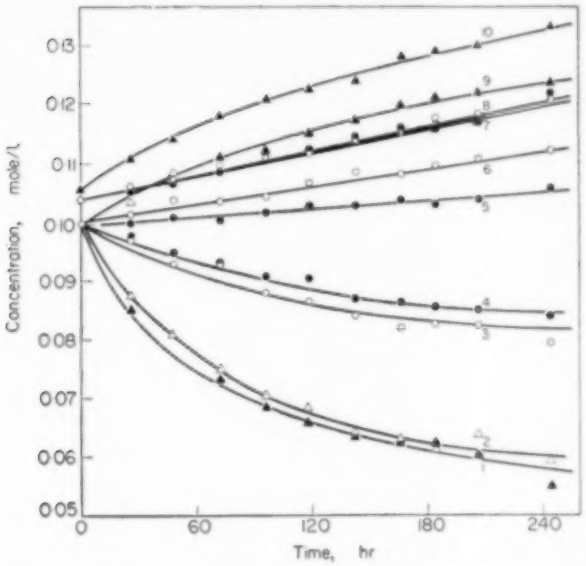



FIG. 2.—Decomposition of 0·1 M HOS solutions at 6·0–6·5° (Curves 1, 2, 3 and 4): ○, HOS, ●, HOS with $H_2SO_4$; △, HOS with NaOH; ▲, HOS with $CuCl_2$. Variations in strong and total acid content are given by Curves 5 through 10.

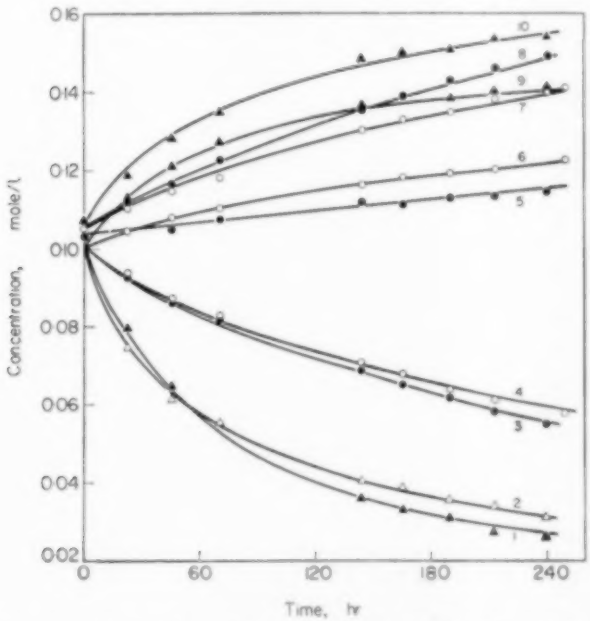



FIG. 3.—Decomposition of 0·1 M HOS solutions at 23·35° (Curves 1, 2, 3 and 4; see legend for Fig. 2). Curves 5 to 10 inclusive represent increases in total and strong acid for each of the respective solutions.

(1) HOS decomposes most rapidly in a solution containing copper(II) ion (1), less rapidly in basic solution (2), even less rapidly in a solution alone (3) and least rapidly of all in an acidic solution (4).
(2) The strong acid, monohydrogen sulphate ion, titer increases most rapidly in the copper-containing solution (9), less rapidly in the solution of HOS alone (6) and least rapidly of all in the solution containing added acid (5).
(3) The change in hydroxylammonium ion concentration (total acid titer less strong acid titer) is greatest in the solution containing added acid (7) whereas the solution of HOS alone (8) exhibits a change in weak acid content almost indentical to that of the copper-containing solution (10).

These observations show that several modes of decomposition are possible for HOS in aqueous solution. The simplest of these, the hydrolysis of HOS to hydroxylammonium ion and monohydrogen-sulphate ions, is enhanced by the presence of additional acid. Other decomposition reactions, not necessarily involving the formation of hydroxylammonium ion, appear to take place to an increasing extent in less acidic solutions and in solutions containing added copper(II) ion. It is also evident that these reactions occur simultaneously, complicating the situation considerably.

The results of identical experiments carried out at 23·35°C are summarized in Fig. 3. The same general behaviour was noted except that the acid-catalysed hydrolysis of HOS appeared to be somewhat more temperature dependent than any of the other reactions. The curves in Fig. 3 represent variations in:

(a) the HOS content of the copper containing solution (1)
(b) the HOS content of the basic HOS solution (2)
(c) the HOS content of the solution containing added acid (3)
(d) the HOS content of the solution of HOS alone (4)
(e) the strong acid titer of HOS with added acid (5)
(f) the strong acid titer of HOS alone (6)
(g) the total acid titer of HOS alone (7)
(h) the total acid titer of HOS with added acid (8)
(i) the strong acid titer of the copper(II) containing solution (9)
(j) the total acid titer of the copper(II) containing solution (10).

To further clarify the situation concerning the decomposition of HOS, the ammonia contents of the solutions of HOS (A) and of HOS with added acid (B) were determined after these solutions had been allowed to stand for several weeks at 23·35°. Ammonia was found in appreciable amounts in both solutions:

| | 501 hr | 838 hr |
|---|---|---|
| Solution A | 0·0102 mole/l. | 0·0112 mole/l. |
| Solution B | 0·0046 mole/l. | 0·0034 mole/l. |

A mass spectrometric analysis of the gaseous decomposition products of HOS solutions allowed to stand at 23·35°C shed additional light upon the decomposition of HOS. The nitrogen : oxygen ratio in these samples was 2·4 : 1 instead of the 4·4 : 1 found in blank determinations and to be expected for air-contamination of the sample. It is evident that oxygen is formed in small quantities during the decomposition of HOS.

When solutions similar to those studied at 6° and 23·35° were refluxed at 100° the HOS was found in each case to have disappeared completely after 2·5 hr. The concentrations of hydroxylamine in the residual solutions were found to be:

Solution A (no additive), 0·07 M
Solution B (containing added $H_2SO_4$), 0·0895 M
Solution C (containing added $Cu^{++}$), 0·0226 M
Solution D (containing added NaOH), 0·003 M

It is again evident that hydrolysis with formation of hydroxylammonium ion is favoured by added $H^+$, but that a decomposition process is favoured in basic solution and is greatly catalysed by added copper ion.

Vol. 12 1959/6

## DISCUSSION

Reactions represented by the following equations can be proposed to account for the various experimental findings:

$$H_2NOSO_3H + H_2O \longrightarrow NH_3OH^+ + HSO_4^- \quad (1)$$

$$3H_2NOSO_3H \longrightarrow N_2 + NH_4^+ + HSO_4^- + 2H_2SO_4 \quad (2)$$

$$2H_2NOSO_3H + 2H_2O \longrightarrow 2NH_4^+ + 2HSO_4^- + O_2 \quad (3)$$

$$2H_2NOSO_3H + 2NH_3OH^+ \longrightarrow 2NH_4^+ + 2HSO_4^- + 2H^+ + N_2O + H_2O \quad (4)$$

In assessing the relative importance of these reactions it is necessary to keep in mind the following experimental facts:

(1) The amount of HOS which decomposes is *always* greater than the net increase in weak acid titer, accountable by formation of $NH_3OH^+$.
(2) The formation of both strong ($HSO_4^-$) and weak ($NH_3OH^+$ and, possibly, $NH_4^+$) acid is influenced markedly by pH.
(3) Ammonia is found in HOS solutions which have been allowed to decompose for several weeks.
(4) Small amounts of oxygen are formed.
(5) The strong acid titer increases much more rapidly than the weak acid titer in the presence of catalytic amounts of Cu(II).

Previous investigators[1,2] have shown that hydroxylammonium ion is formed when HOS undergoes hydrolysis. The weak acid titer increases most rapidly in those solutions containing added acid, thus confirming semi-quantitatively the findings of HARNSBERGER and MORONEY[11] who came to the conclusion that the hydrolysis process is acid-catalysed. Equation (3) represents a second avenue of decomposition which, like process (1), would cause no change in the strong acid titer. For both of these processes one mole of strong acid ($HSO_4^-$) is formed for each mole of HOS undergoing decomposition. Reaction (3), which assumes that decomposition could occur through solvolysis of a Caro's acid intermediate ($H_2NOSO_3H \longrightarrow HOOSO_3H$), is believed to be of only minor importance and could account for the formation of some oxygen during the decomposition process. Reaction (1) is therefore believed to be the predominant reaction in solutions of HOS and those containing added acid.

Reactions (2) and (4) illustrate decomposition schemes which would cause an increase in both strong acid titer and in total acidity. Check experiments showed that HOS and hydroxylamine salts do react in boiling solutions. Particularly significant, however, is the experimental finding that the presence of Cu(II) ion causes decomposition to occur with a great increase in strong acid content, but only a small change in weak acid concentration. In other words, solutions of HOS containing added Cu(II) ion undergo decomposition largely by a route which does not allow any build-up of $NH_3OH^+$ in solution. This observation suggests that one or more redox reactions are taking place in which Cu(II) ion is exerting a marked catalytic effect (as it does in the autoxidation of $NH_2OH$[14] and of hydrazine[15]. The reaction represented by (2) is essentially similar to the disproportionation process which had been

[14] P. C. MOEWS and L. F. AUDRIETH, *J. Inorg. Nucl. Chem.* In press.
[15] L. F. AUDRIETH and P. H. MOHR, *Industr. Engng. Chem.* **43**, 1774 (1951).

observed by SOMMER[2] to take place in alkaline solution. It is completely similar to the self-oxidation reduction processes which occur whenever potential imide donors undergo decomposition in accordance with the following type equation:[16]

$$3HN(A) \longrightarrow N_2 + NH_3 + 3A$$

where HN(A) = chloramine ($HN{\cdot}HCl$), hydrogen azide ($HN{\cdot}N_2$), hydrazine ($HN{\cdot}NH_3$), hydroxylamine ($HN{\cdot}H_2O$) and now HOS as $HN{\cdot}H_2SO_4$.

It is evident from the experimental results presented above that reactions (1) and (2) dominate in the decomposition of HOS in aqueous media. The hydrolytic process given by equation (1) is an acid catalysed process. SOMMER[2] has shown that (2) becomes the dominant process as the pH of the solutions is raised, but reaction (2) takes place to a limited extent even in acid solutions and particularly in those systems containing catalytic amounts of dissolved copper. Reactions (3) and (4) are believed to play only minor roles in those reactions which influence the stabilities of aqueous solutions of HOS.

It should be emphasized again that HOS and chloramine are similar in many respects. The reactions set forth above are completely analogous to those proposed by AUDRIETH and ROWE[16] in their study of the factors which affect the stabilities of chloramine solutions. Both substances are oxidizing agents; both substances serve as aminating agents particularly in their reactions with ammonia and amines to give hydrazine and N-substituted hydrazines. Aqueous solutions undergo analogous decomposition processes involving both hydrolysis and disproportionation. In each case the latter process is markedly accelerated by the catalytic effect of traces of dissolved copper.

Vol.
12
1959/60

*Acknowledgement*—Support of this investigation by the Office of Ordnance Research, Contract DA-11-022-ORD-828, is acknowledged with gratitude.

[16] L. F. AUDRIETH and R. A. ROWE, *J. Amer. Chem. Soc.* **77**, 4726 (1955).

J. Inorg. Nucl. Chem., 1959, Vol. 12, pp. 193 to 198. Pergamon Press Ltd. Printed in Great Britain.

# THE ADSORPTION OF INORGANIC SALTS BY AMINE RESINS FROM ORGANIC SOLVENTS

J. KENNEDY and R. V. DAVIES
Atomic Energy Research Establishment, Harwell, Berkshire, England

(*Received* 10 *March* 1959)

**Abstract**—The adsorption of lithium, cupric and cobaltous chlorides, and of nickel nitrate from organic solvents by anion-exchange resins has been investigated. Adsorption by the basic form of the tertiary amine resin Deacidite H takes place through complex formation with the resin functional groups, and both cation and anion are adsorbed in equivalent proportions. Increased crosslinking (per cent nominal divinyl benzene) of Deacidite H from 1 to 9 per cent has little effect on the uptake of lithium chloride, but a significant reduction is observed in cobalt chloride adsorption for cross-linking greater than 2 per cent. Adsorption is influenced by the nature of the solvent, and is much greater from acetone than from dimethyl formamide.

THE literature on ion-exchange and adsorption of salts on synthetic resins from non-aqueous media is very limited compared with the extensive literature for aqueous systems. The scarcity of data is understandable, as the need to remove salts from organic solvents other than by back-extraction with an aqueous phase rarely arises. However, with the growing interest in the solution chemistry of salts in organic systems, and the desire to extend the number of potential separation methods, occasions may arise (or can be anticipated) where it would be advantageous to conduct separations of salts in an organic medium or to remove them completely from the organic solvent under strictly anhydrous conditions. Where it is desirable, for economic reasons, to recover large quantities of solvents such as acetone or dimethyl formamide, the solubility of which in water prevents the use of the latter for back-extraction, adsorption of the salt on an insoluble solid phase would avoid an expensive distillation and the wastage which would otherwise result from pyrolysis of the solvent; in addition, side reactions during distillation are eliminated. Furthermore, the adsorbed metals may be eluted directly and in a pure state from the solid phase.

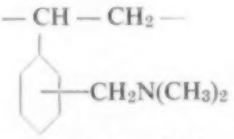
The desalting of organic solvents by dual or mixed beds of acidic and basic ion exchangers can be shown to be feasible from the data available on the behaviour of the latter in organic systems,[1] but the rate of exchange compared to that in water is greatly reduced as a result of the low degree of ionization under non-aqueous conconditions. KATZIN and GEBERT have shown[2] that rapid adsorption of a number of salts from acetone takes place on the chloride form of a strongly basic resin, but while the adsorption coefficients were very high in favour of the resin, and both cation and anion were simultaneously adsorbed, the presence of water in the resin phase was necessary for adsorption to occur. Though such a procedure would be

[1] O. D. BONNER, *J. Chem. Educ.* **34**, 174 (1957).
[2] L. I. KATZIN and E. GEBERT, *J. Amer. Chem. Soc.* **75**, 801 (1953).

sufficient to remove salts from acetone and possibly from other solvents, it would hardly be desirable for the recovery of solvents in a completely anhydrous state.

As part of a programme designed to this end, the applicability of non-ionic phosphorylated polymers such as tri-allyl phosphate, $[(C_3H_5O)_3P(O)]_n$, to salt extraction from anhydrous acetone and alcohol has already been demonstrated.[3] However, the relatively weak co-ordinating power of the phosphoryl oxygen in such a polymer for transition elements renders it ineffective as an extractant from more basic strongly co-ordinating solvents such as dimethyl formamide. As previously emphasized,[3] a resin of the phosphine oxide type, $[R_3P(O)]_n$, might be applicable to the extraction of salts from strongly solvating media because of the enhanced basicity of the phosphoryl oxygen, but the very limited effort on our part to synthesize such a polymer was unsuccessful.[4]

An obvious alternative to any of the above resins is commercially-available Deacidite H, which has the following structure:



The high affinity of amine resins for cupric salts has already been demonstrated, although no details are given.[5] This paper describes a more detailed investigation of the application of Deacidite H for desalting acetone and dimethyl formamide. In addition some emphasis has been laid on the effect of resin crosslinking on its salt uptake. The adsorption of salts under similar conditions by the strongly basic quaternary ammonium resin Deacidite FF was also investigated.

Vol. 12 1959/6

## EXPERIMENTAL

*Resins*

The resins were obtained in the chloride form from the Permutit Co. Ltd., London. They were twice recycled with one hundred bed volumes of 0·5 N NaOH, water, 0·5 N HCl, 0·5 N NaOH, and water in that order, and were finally washed exhaustively with carbonate-free distilled water, after which they were dried and stored in the basic form over silica gel. Portions of the resins thus treated were also converted to the chloride form. Capacities were determined by shaking portions ($\frac{1}{2}$ g) for 48 hr with 50 ml N/10 HCl, filtering, and back-titrating the filtrate with standard alkali. On heating basic Deacidite H resins for 3 hr at 100° under vacuum, in order to remove strongly-basic quaternary ammonium groups,[6] the capacities were not significantly changed, indicating that the contribution of these groups to the total exchange capacity was less than 3 per cent. Capacities and crosslinking (% nominal divinyl benzene (DVB) content) are given in Table 1.

*Solutions*

Stock solutions (0·04 M) were prepared of LiCl, $CoCl_2$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $Ni(NO_3)_26H_2O$ in both anhydrous redistilled dimethyl formamide (DMF) and in acetone. The solutions were finally assayed for lithium with an EEL flame photometer and colorimetrically[7] for the other metals. $Ni(NO_3)_2 \cdot 6H_2O$ was used instead of $NiCl_2$ because of the low solubility of the latter in acetone. The chloride content of the solutions was determined by precipitation as silver chloride, followed by dissolution in ammonia and colorimetric analysis of the silver using sodium sulphide.[8]

[3] J. KENNEDY, *J. Appl. Chem.* **9**, 26 (1959).
[4] J. KENNEDY, E. S. LANE and B. K. ROBINSON, *J. Appl. Chem.* **8**, 459 (1958)
[5] D. A. ROBINSON and G. F. MILLS, *Industr. Engng. Chem.* **41**, 2221 (1949).
[6] J. AVESTON, D. A. EVEREST and R. A. WELLS, *J. Chem. Soc.* 231 (1958).
[7] E. B. SANDELL, *Colorimetric Determination of Traces of Metals* pp. 279, 304, 475. Interscience, New York (1950).
[8] F. SNELL and C. SNELL, *Colorimetric Methods of Analysis* p. 533. Van Nostrand, New York (1954).

*Equilibration*

Portions of the resins (½ g) were shaken for 16 hr with solutions (50 ml) of varying initial salt concentration (0·04–0·004 M) in acetone and DMF. Equilibrium was always attained in less than 3 hr, and acetone solutions of the coloured salts which were contacted with Deacidite H and moist Deacidite FF became lighter in colour during equilibration, or colourless in the case of the initially more dilute solutions, accompanied by a progressive colouration of the resins. The equilibrated solutions were filtered, their metal content was determined, and the metal adsorbed on the resin was determined by difference. The chloride content of the equilibrated lithium, cobaltous and cupric solutions was also determined.

TABLE 1.—RESIN PROPERTIES

| | Deacidite H | | | | Deacidite FF |
|---|---|---|---|---|---|
| Crosslinking:—<br>(% Nominal DVB) | 1 | 2 | 3½ | 9 | Commercial grade |
| Capacity m equiv/g dry basic resin | 3·5 | 5·3 | 4·8 | 3·7 | 4·1 |

## RESULTS AND DISCUSSION

*General*

The ratio of metal to chloride in the equilibrated chloride solutions was invariably the same as in the original salt, indicating that in the instances where adsorption occurred both cation and anion were adsorbed in equivalent proportions. The removal of both ions from solution was also demonstrated by testing portions of the effluent from columns of the resins after passage of solutions of the salts in acetone or DMF. The salts could then be completely removed from the columns by elution with 10–15 bed volumes of N/10 HCl.

TABLE 2.—DISTRIBUTION COEFFICIENTS OF LITHIUM CHLORIDE BETWEEN MOIST DEACIDITE FF (CHLORIDE FORM, WATER CONTENT 18·5%) AND ORGANIC SOLVENTS

| Solvent | Initial concentration of LiCl (M) | Distribution coefficient $K_d$* |
|---|---|---|
| Acetone | 0·04 | 124 |
| Dimethyl formamide | 0·04 | 18 |

$$* K_d = \frac{\text{millimoles adsorbed per gramme of resin}}{\text{millimoles per ml in solution at equilibrium}}$$

*Adsorption of salts by Deacidite FF*

No adsorption of lithium chloride from acetone or DMF takes place with the anhydrous chloride or with the hydroxyl form of the strong-base resin Deacidite FF. The adsorption of the salt from moist Deacidite FF (chloride form) from the same solvents is given in Table 2. Adsorption of the salt from acetone is consistent with the results of KATZIN and GEBERT[2]. The most likely explanation for adsorption by moist, strongly-based resins (when precipitation or the possibility of adsorption through complex formation is excluded) is that advanced by DAVIES and OWEN,[9] who

[9] C. W. DAVIES and B. D. R. OWEN, *J. Chem. Soc.* 1676 (1956).

suggest that adsorption under these conditions is due to preferential solution of the salts in the aqueous phase present in the resin. The high retention of water by the resin (which is strongly hydrophilic compared with acetone) would result in very little dilution by the organic phase of the water present in the resin and the organic solvent would virtually remain anhydrous.[9] Separate experiments have also shown that a moist sulphonic acid resin (Zeokarb 225 $H^+$ and $K^+$ forms) adsorbs both cation and anion from acetone solutions of cobaltous and lithium chlorides. The relatively low adsorption coefficients obtained with DMF (Table 2) and by KATZIN and GEBERT[2] with tertiary butyl alcohol probably result from partial dehydration of the resin phase by these solvents combined with their greater tendency towards salt solvation compared with ketones.

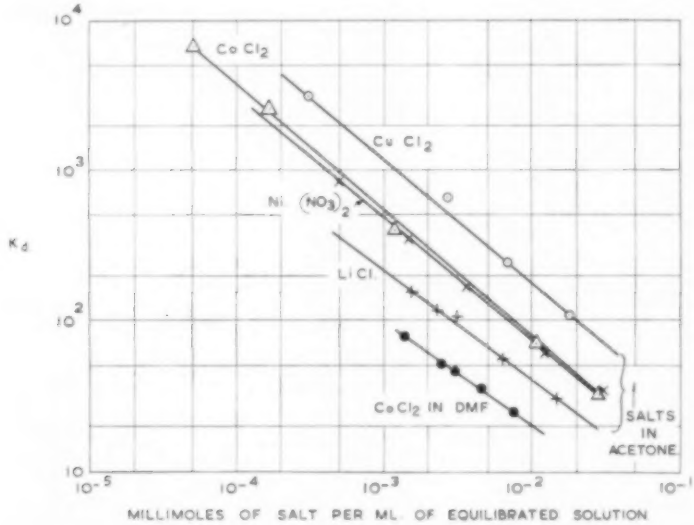



FIG. 1.—Adsorption of salts from anhydrous acetone and from dimethyl formamide by Deacidite H (1% DVB).

*Adsorption of salts by Deacidite* H

$K_d$ values for LiCl, $CoCl_2$, $CuCl_2 2H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ are plotted in Fig. 1 as a function of the equilibrium concentration in acetone.

No change in $K_d$ resulted when $CoCl_2 \cdot 6H_2O$ was substituted for the anhydrous salt in these experiments or when a moist Deacidite H resin (water content 13·7 per cent) was substituted for the dry resin in the case of LiCl. High and inconsistent values of $K_d$ were obtained with $CoCl_2$ and the moist resin, probably due to precipitation of cobaltous hydroxide. As with Deacidite FF, no adsorption takes place on the dry chloride form of Deacidite H.

These results indicate that adsorption on dry Deacidite H occurs as a result of the formation of amine complexes between the resin functional groups and the salt, i.e.

$$\alpha\, R\, Me_2N + MX_p \rightleftharpoons (R\ Me_2N)_\alpha MX_p$$

Vol. 12 1959/6

where $R(Me)_2N$ represents the repeating polymeric unit. The mass action equilbrium coefficient ($K_c$) for this reaction is

$$K_c = \frac{[(RMe_2N)_xMX_p]}{[RMe_2N]^x[MX_p]} = K_d/[RMe_2N]^x$$

from which $\log K_d = K_c + x \log [RMe_2N]$.

Attempts were made to use this equation to evaluate $x$, by using different possible values 1–4 to obtain corresponding concentrations of the uncomplexed resin $[RMe_2N]$ from the total resin concentration and the concentration of adsorbed salt, but these were unsuccessful. This is not surprising in view of the high loadings on the resin and the resulting deviations from thermodynamic ideality in the resin phase. It is probable also that $x$ varies with the mole fraction of the free resin, and that variable amounts of solvent may be included along with the resin amine ligands and anions in the co-ordination sphere of the adsorbed metal. The adsorption sequence Cu > Co > Li is however consistent with the stability sequence for monomeric complexes with the same metals[10] but the adsorption sequence Co ≧ Ni is the reverse of the normal order and may result from the use of the nitrate rather than the chloride in the case of nickel.

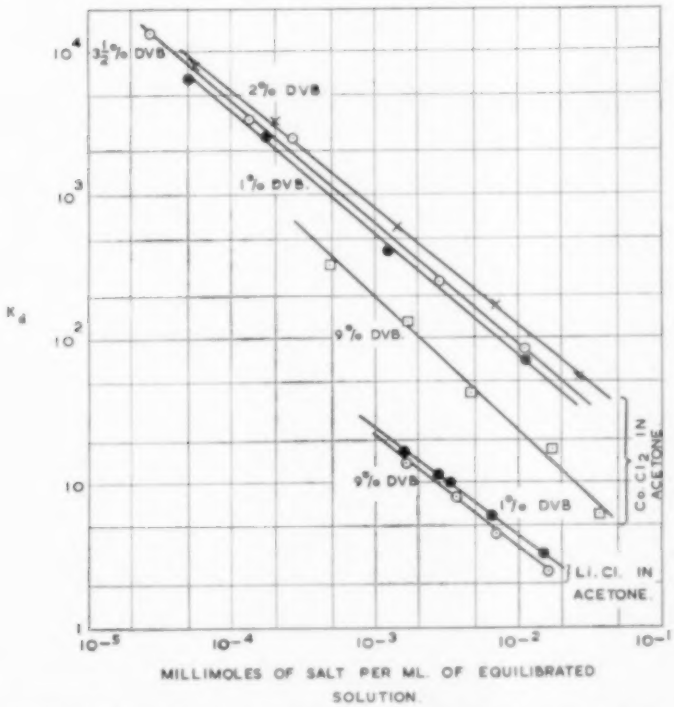



FIG. 2.—Effect of crosslinking (% DVB) on the adsorption of lithium and cobaltous chlorides from acetone by Deacidite H.

[10] A. E. MARTELL and M. CALVIN, *Chemistry of the Metal Chelate Compounds*. Prentice-Hall, New York (1953).

*Effect of crosslinking*

$K_d$ values for LiCl and $CoCl_2$ as a function of equilibrium salt concentrations using Deacidite H resins of varying nominal DVB content are given in Fig. 2. $K_d$ values for LiCl with resins of 2 and $3\frac{1}{2}\%$ DVB content are not included but are intermediate between those of 1 and 9% DVB and almost coincident with each other. The variation in the resin capacity (Table 1) renders comparison difficult, although it is significant that while $K_d$ values for $CoCl_2$ increase perceptibly between 1 and 2% DVB and then drop considerably between 2 and 9% DVB, those for LiCl vary but slightly with DVB content. This effect is understandable from a consideration of the relative molecular dimensions of the two salts.

*Adsorption by Deacidite* H *from* DMF *solutions*

$K_d$ values for $CoCl_2$ in DMF as a function of equilibrated solution concentration are given in Fig. 1. No absorption of LiCl was detected by dry or moist Deacidite H (13·7% $H_2O$) under these conditions. The reduced $K_d$ values obtained with DMF compared with acetone are expected in view of the greater basicity and solvating power of amides compared to ketones.

Comparison of the results obtained in these series of experiments with those obtained elsewhere[3] using polymeric triallyl phosphate indicates that the latter is more effective than the tertiary amine resin Deacidite H for adsorbing lithium salts from solution, while the reverse is true in the case of cobalt salts. These observations are consistent with the affinity sequence of oxygenated and amine ligands for alkali and divalent transition metals.[10]

*Acknowledgements*—We are grateful to the Permutit Co. Ltd., London, for supplying Deacidite H resins, and to Mr. B. K. ROBINSON for assistance in some of the experimental work.

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1959, Vol. 12, p. 199. Pergamon Press Ltd. Printed in Great Britain.

# BOOK REVIEW

GLENN T. SEABORG: **The Transuranium Elements.** Yale University Press, 1958. 328 pp., $7.00.

THIS remarkable and fascinating book grew out of the Silliman Lectures which the author gave at Yale University in May 1957. It covers a great deal of interesting material, ranging from a historical summary of the early plutonium project to a rather critical survey of some advanced topics in nuclear chemistry and physics.

A very interesting part is Chapter I, "The Plutonium Story" wherein Dr. SEABORG has arrived at a kind of chemist's Symth Report, which not only gives a historical account of those hectic and exciting early times of the Manhattan project but also recaptures some of the flavour of the then new science which was developing day by day. Amusing incidents contribute to the authenticity. Speaking of the classification difficulties with plutonium and neptunium he relates: " . . . I recall that a code name was often used for element 94, even in oral references. Throughout 1941 we referred to it by the code name of 'copper', which was all right until we found it necessary to introduce the element copper into some of our experiments, . . . For a while we referred to plutonium as 'copper' and the real copper as 'honest-to-God copper'."

Step by step the laborious path towards isolation of weighable plutonium was made. ". . . numerous visitors came to our laboratory to have a look at the fascinating new element. With the supply so limited and the experiments to be performed so many, it was not possible to keep much material immobilized to show them. It is, therefore, with some hesitation that we may now confess that some of the (plutonium) hydroxide samples which were placed on view consisted of the much more available aluminum hydroxide colored with green ink; . . ." You will find the complete story from discovery to production and application authoritatively chronicled here.

Chapter II, on the chemical properties of the actinides, is a review of the chemistry of this group of elements, remarkably detailed, and at the highest level. It should be very helpful as a teaching aid to senior and graduate courses in inorganic chemistry as well as those attempting to keep up on this field.

Chapter III contains enough nuclear chemistry for part of a course and might well serve as a text or supplementary reading at a level just beyond radiochemistry. It is, therefore, probably addressed to a more limited audience. However, if anyone still wonders what all the excitement is about in heavy elements, just glance at how much has been observed about nuclear phenomena by use of these synthetic elements which otherwise might never have been possible.

In Chapter IV Chancellor SEABORG discusses the even more difficult problems ahead in the discovery of further new elements. Whole new concepts of chemical separations and identifications must be developed as this frontier is extended further. However, there is little doubt that as many fascinating phenomena yet remain to be discovered in this field as have already been observed.

By now it is clear that my suggestion to everyone interested in science is to read as much of this book as possible. Some part of it will be of interest to historians, teachers, scientists and perhaps even administrators and one or two retired Professors of Inorganic Chemistry.

*Purdue University* JAMES W. COBBLE

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 201 to 205. Pergamon Press Ltd. Printed in Northern Ireland

# IDENTIFICATION OF $^{142}$Xe AND MEASUREMENT OF ITS CUMULATIVE YIELD FROM THERMAL-NEUTRON FISSION OF $^{235}$U*

K. WOLFSBERG, D. R. NETHAWAY, H. P. MALAN† and A. C. WAHL
Department of Chemistry, Washington University, St. Louis, Missouri

(*Received* 17 *February* 1959)

**Abstract**—$^{142}$Xe has been identified as a product of the thermal-neutron fission of $^{235}$U by determination of 85 min $^{142}$La in the active deposit of highly emanating uranyl stearate. The half-life of $^{142}$Xe is ~1·5 sec, and its cumulative yield in fission is 0·059 $\left(\begin{smallmatrix}+0.006\\-0.003\end{smallmatrix}\right)$ of the total 142-chain yield. The cumulative yield of $^{141}$Xe has been redetermined to be 0·205$\left(\begin{smallmatrix}+0.019\\-0.004\end{smallmatrix}\right)$of the 141-chain yield, in agreement with the previously reported value of 0·21 ± 0·02. The $^{145}$Xe yield is compared with values predicted by various postulates of nuclear charge distribution in fission.

The mass number of the 85 min La has been proven to be 142 by its formation from the $^{140}$Ce-$(n,p)^{142}$La reaction.

MANY of the short-lived krypton and xenon fission products were identified and their half-lives measured by gas-sweeping experiments in which descendants were determined in the active deposit.[1] Later, cumulative yields were measured by an emanation technique involving quantitative escape of the inert gases from barium stearate and determination of their descendants.[2] However, due to the difficulty of isolating 85 min $^{142}$La, $^{142}$Xe was not identified, nor was its yield measured.

Ion-exchange procedures have now been developed which make possible the isolation of $^{142}$La. They have been used with a modified emanation technique[3] to identify $^{142}$Xe and to measure its cumulative yield.

## EXPERIMENTAL

The emanating material used was uranyl stearate, which emanates 10 sec $^{91}$Kr and 3 sec $^{92}$Kr as efficiently[2] as does barium stearate. The uranyl stearate was prepared from aqueous solutions of sodium stearate and uranyl nitrate (enriched to 20 per cent in $^{235}$U) by a procedure that has been described.[4] Approximately 300 mg were placed in an aluminium cup in the base of an aluminium irradiation container of the same design as the one used previously.[2]

Irradiations were performed at the Washington University Cyclotron. Neutrons were produced by the $^{9}$Be$(d,n)^{10}$B reaction and were moderated by ~9 in. of paraffin. At the position of the irradiation container a thermal-neutron flux of $\sim 7 \times 10^{7}$ cm$^{-2}$ sec$^{-1}$, with a cadmium ratio of 80,‡ was

* This work was done under the auspices of the United States Atomic Energy Commission.

† Present address: University of Stellenbosch, Cape Province, Union of South Africa.

‡ The cadmium ratio was measured by determination of $^{97}$Zr from fission of the uranium enriched to 20 per cent in $^{235}$U.

[1] E. L. BRADY and N. SUGARMAN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 613. McGraw-Hill, New York (1951); C. R. DILLARD, R. M. ADAMS, H. FINSTON and A. TURKEVICH, *Ibid.* p. 616; R. OVERSTREET and L. JACOBSON, *Ibid.* p. 621; C. R. DILLARD, R. M. ADAMS, H. FINSTON and A. TURKEVICH, *Ibid.* p. 624.

[2] A. C. WAHL, *J. Inorg. Nucl. Chem.* **6**, 263 (1958).

[3] K. WOLFSBERG and A. C. WAHL. Unpublished work.

[4] A. C. WAHL and W. R. DANIELS, *J. Inorg. Nucl. Chem.* **6**, 278 (1958).

obtained with a 200 $\mu$A deuteron beam. About $3 \times 10^8$ fissions occurred during a 30 min irradiation. The inert-gas fission products emanated from the uranyl stearate powder and decayed in the evacuated space above, depositing their descendants on a filter-paper liner.[2]

After an irradiation the filter-paper liner and the uranyl stearate were dissolved separately in ~25 ml of fuming nitric acid containing lanthanum and cerium carriers, ~4 ml of 70% $HClO_4$ were added, and the resulting solutions evaporated to fumes of $HClO_4$.

*Anion-exchange procedure for lanthanum*

The carriers added were 2 mg of lanthanum and 3 mg of cerium. $LaF_3$ and $CeF_3$ were precipitated from acid solution, washed with dilute HF, and dissolved in a $H_3BO_3$–$HNO_3$ mixture.[5] Cerium was oxidized by $BrO_3^-$ and extracted from 10 M $HNO_3$ into 0·75 M di(2-ethyl hexyl)orthophosphoric acid in n-heptane.[6] $La(OH)_3$ was precipitated from the aqueous phase by $NH_4OH$, washed with water, and dissolved in 0·25 M HCl. This solution was contacted with 1·5 M di(2-ethyl hexyl)orthophosphoric acid in toluene for removal of yttrium and the heavier rare earths.[7] $La(OH)_3$ was precipitated from the aqueous phase by $NH_4OH$, washed with water, and dissolved in one drop of 6 M HCl. The solution was evaporated to dryness, and the $LaCl_3$ was dissolved in one drop of 4 M $NH_4CNS$. This solution was transferred to a Dowex 1-X2 resin column in the $CNS^-$ form. The resin bed was 3 mm in diameter and ~7 cm long. Elution by 2 M $NH_4CNS$ at 0·02 to 0·025 ml/min removed the lanthanum ahead of praseodymium.[8] The break-through point was detected with a portable Geiger counter and occurred after 0·7 to 1·0 ml of the eluant had passed through the resin bed. Thereafter the radioactivity of each drop was measured. Those in the lanthanum peak (0·15 to 0·20 ml) were combined, and $La_2(C_2O_4)_3$ was precipitated and mounted as a slurry and dried on a polyethylene disk.

Duplicate samples were run in less than 3 hr after the initial fuming operations were completed. The chemical yield was ~25 per cent. It was determined, after decay of the lanthanum activities, by neutron activation of the ~0·5 mg of lanthanum on the polyethylene disk. A small amount of an unknown long-lived contaminant appeared in some of the samples.

*Cation-exchange procedure for lanthanum*

The carriers added before dissolution of the filter paper and uranyl stearate were 10 mg of lanthanum and 0·2 mg of cerium. Immediately after the fuming operation (~25 min after the end of an irradiation) barium carrier was added, and $BaSO_4$ was precipitated to remove the remaining 18 min $^{141}$Ba and 11 min $^{142}$Ba from the two samples at the same time and to reduce somewhat the contribution of $^{141}$La to the complex decay curves. $LaF_3$ was then precipitated from acid solution, washed with dilute HF solution, and dissolved in a $H_3BO_3$–$HNO_3$ mixture.[5] $La(OH)_3$ was precipitated by $NH_4OH$, and dissolved in concentrated HCl. The solution was passed through a Dowex 1 anion exchange column to remove elements forming anionic chloride complexes, e.g. zirconium and niobium.[9] $La(OH)_3$ was again precipitated, washed, and dissolved in one drop of concentrated HCl. After dilution of the solution to 30 ml the rare earth elements were adsorbed on 0·25 cc of Dowex 50W cation exchange resin. The resin was centrifuged and transferred to the top of a Dowex 50W column 4 mm in diameter and 20 cm long. Lanthanum was separated from the other rare earths by selective elution at ~90°C with 1·0 M ammonium lactate (pH = 3·32) at ~0·017 ml/min.[10] Samples were collected during 4 min intervals, and peaks were observed by precipitation of cerium or lanthanum oxalates. After the cerium peak there was an ~0·07 ml gap before the start of the lanthanum peak. As the lanthanum appeared (~40 min after the start of the elution) the flow rate was increased ~50 per cent, and all the lanthanum was collected during the next 20 min. The $La_2(C_2O_4)_3$ was collected on Whatman No. 50 filter paper, dried, mounted on cardboard, covered with No. 850 Scotch tape, and counted.

Vol. 12 1959/6

[5] N. E. BALLOU, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 1673. McGraw-Hill, New York (1951).
[6] D. F. PEPPARD, G. W. MASON and S. W. MOLINE, *J. Inorg. Nucl. Chem.* **5**, 141 (1957).
[7] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[8] J. P. SURLS, JR. and G. R. CHOPPIN, *J. Inorg. Nucl. Chem.* **4**, 62 (1957).
[9] K. A. KRAUS and F. NELSON, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, pp. 113–125. United Nations (1956).
[10] See for example, W. E. NERVIK, *J. Phys. Chem.* **59**, 690 (1955).

Duplicate samples were completed in about 2½ hr after the end of an irradiation. The chemical yield was ~65 per cent. It was determined after measurements of radioactivity were completed by ignition of the $La_2(C_2O_4)_3$, filter paper, and Scotch tape to constant weight. The ash from the filter paper and Scotch tape was negligible. There was no evidence of radioactive contamination in the samples.

The measurements of radioactivity were made with a side-window, methane-flow, $\beta$-proportional counter. The activities due to $^{141}La$ and $^{142}La$ were resolved by an analytical method[11] after subtraction of low-intensity, long-lived components due to $^{140}La$ and $^{141}Ce$. The observed half-lives of $^{141}La$ and $^{142}La$ were in good agreement with the 231 min and 85 min values reported by SCHUMAN *et al.*[12] Corrections for radiation absorption and scattering and counting efficiency were negligible because the two samples to be compared were of nearly equal weights, were mounted in the same way, and were counted on the same counter.

For calculation of a cumulative yield, the activities of the two samples at the same arbitrary time were corrected for chemical yield, for loss of uranyl stearate during transfer from the irradiation container (~2 per cent, determined by weighing), and for the ~2 per cent active deposit not collected.[2] The cumulative yield, expressed as a fraction of the total chain yield, was obtained by division of the corrected lanthanum activity from the active deposit by the sum of the lanthanum activities from the two samples and multiplication by 1·015 (correction for decay of xenon in the evacuated space between the uranyl stearate grains). It was assumed that the emanating power of the uranyl stearate for the xenon isotopes was 100 per cent and that no appreciable fractions of the chains were formed independently after lanthanum. The assumptions are discussed later.

## RESULTS

In the first two runs the anion-exchange procedure for lanthanum was followed. The decay curves for all samples contained the 85 min $^{142}La$ component showing that $^{142}Xe$ exists and that it is formed in fission.

The absolute values for the $^{142}Xe$ cumulative yield calculated from the data for these runs are not considered reliable because the yields calculated for $^{141}Xe$ do not agree, indicating some error in the analysis, and because a batch of uranyl stearate was used that emanated only ~90 per cent of 3·0 sec $^{92}Kr$. However, the measured ratios of the $^{142}Xe/^{141}Xe$ fractional cumulative yields (0·24 and 0·32) may be significant if the emanating power of the uranyl stearate was the same for the two isotopes. These ratios combined with the published value[2] for the $^{141}Xe$ yield (0·21 ± 0·02 of the total chain yield) give 0·051 and 0·066 for the fractional chain yield of $^{142}Xe$, in fair agreement with the more accurately measured values discussed below.

The results obtained with uranyl stearate that emanated[3] 99 ± 3 per cent of 3·0 sec $^{92}Kr$ are summarized in Table 1. The cation-exchange procedure for lanthanum was followed.

As can be seen from Table 1 the precision of the measurements was excellent. The agreement between the $^{141}Xe$ values calculated from the lanthanum and from the cerium activities shows that the samples contained no appreciable radioactive contaminants. The estimated uncertainties in the average values due to errors in the measurements are ~5 per cent for $^{142}Xe$ and ~2 per cent for $^{141}Xe$. These estimates do not include a possible systematic error due to non-quantitative emanation, which would make the measured values low. The magnitude of such an error would depend on the half-lives of the inert gases.

The half-life of $^{141}Xe$ is 1·7 sec.[13] An approximate value for the half-life of $^{142}Xe$ was estimated from the results of an emanation experiment at atmospheric

[11] See for example, W. F. BILLER, UCRL-2067 (1953) Unpublished; A. C. WAHL, *Phys. Rev.* **99**, 730 (1955).
[12] R. P. SCHUMAN, E. H. TURK and R. L. HEATH, *Bull. Amer. Phys. Soc.* Ser. II, **3**, 315 (1958).
[13] S. KATCOFF and A. GOLDSTEIN, U.S.A.E.C. Document MDDC-293 (1946) Unpublished.

pressure. Compared to the experiments conducted in vacuum, the escape of the 142-chain was reduced by a factor of 1·84, only slightly more than the factor of 1·70 for the 141-chain. Since the lower emanating power at atmospheric pressure is due to the successful competition of the rate of decay of xenon with the rate of diffusion of xenon in air,[4] the half-life of $^{142}$Xe must be only a little less than the half-life of $^{141}$Xe, say $\sim$1·5 sec.

Since the uranyl stearate used emanated $>$96 per cent of the 3·0 sec $^{92}$Kr, the time spent by krypton in the uranyl stearate must be $<$0·17 sec. If the time spent by xenon

TABLE 1.—CUMULATIVE YIELDS OF $^{142}$Xe AND $^{141}$Xe

| Run | Cumulative yield, fraction of total chain yield | | |
|---|---|---|---|
| | $^{142}$Xe | $^{141}$Xe | $^{141}$Xe* |
| 1 | 0·060 | 0·208 | 0·201 |
| 2 | 0·059 | 0·205 | 0·205 |
| 3 | 0·059 | 0·203 | 0·206 |
| Average | 0·059 | 0·205 | 0·204 |

* Calculated from $^{141}$Ce activities that grew into the lanthanum samples.

in the uranyl stearate is taken to be $<$0·2 sec, more than 91 per cent of a 1·5 sec xenon isotope would have escaped. Therefore, the average values in Table 1 should not be low by more than 9 per cent.

In support of the assumption that negligible fractions of the 142- and 141-chains are formed independently after lanthanum, these fractions are estimated to be $5 \times 10^{-3}$ and $4 \times 10^{-5}$, respectively, from the normal charge distribution curve[2] positioned to fit the xenon yields.

The values and errors chosen for the $^{142}$Xe and $^{141}$Xe fractional cumulative yields are $0{\cdot}059\left(\begin{smallmatrix}+0{\cdot}006\\-0{\cdot}003\end{smallmatrix}\right)$ and $0{\cdot}205\left(\begin{smallmatrix}+0{\cdot}019\\-0{\cdot}004\end{smallmatrix}\right)$, respectively. The latter value is in agreement with the value of $0{\cdot}21 \pm 0{\cdot}02$ determined by WAHL[2] using barium stearate.

## DISCUSSION

The experimental value for the $^{142}$Xe cumulative yield is compared in Table 2 with those predicted by various postulates of nuclear charge distribution in fission. The usual charge distribution curve[2,14,15] for a chain has been used with the most probable charge ($Z_p$) values predicted by the postulates.

The cumulative yield predicted by the postulate of maximum energy release is not in agreement with the experimental value. However, the various forms of the equal charge displacement hypothesis and the empirical $Z_p$ curve give reasonably good predictions. The $^{141}$Xe cumulative yield value was also predicted with reasonably

[14] L. E. GLENDENIN, C. D. CORYELL and R. R. EDWARDS, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 489. McGraw-Hill, New York (1951).

[15] A. C. PAPPAS, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva* 1955. Vol. 7, pp. 19–26. United Nations (1956).

Vol. 12 1959/6

accuracy[2] by the equal charge displacement postulate and was used in the construction of the empirical $Z_p$ curve.

The mass number of the 85 min lanthanum has been proven to be 142 by its

TABLE 2.—COMPARISON OF EXPERIMENTAL AND PREDICTED $^{142}Xe$ CUMULATIVE YIELDS

| Postulate | | Cumulative yield, fraction of total chain yield |
|---|---|---|
| (Experimental) | | 0·059 |
| Equal Charge Displacement | (G., C. and E.)[16] | 0·12 |
| | (PAPPAS)[15] | 0·12 |
| | (S. and G.)[16] | 0·07 |
| | (G. and M.)[17] | 0·07 |
| Empirical $Z_p$ curve[2] | | 0·10 |
| Maximum energy release[17] | | 0·40 |

formation from the $^{142}Ce(n,p)^{142}La$ reaction. Samples of cerium of normal isotopic composition (11·08 per cent $^{142}Ce$) and cerium enriched to 83·42 per cent in $^{142}Ce$ were irradiated together in the fast-neutron flux produced by 10·5 MeV deuterons on beryllium at the Washington University Cyclotron. The yields of the 85 min lanthanum per millimole of $^{142}Ce$ from the two samples were equal. The energy of the fast neutrons was less than the threshold energy calculated for the $^{142}Ce(n,d)^{141}La$ reaction.

[16] E. P. STEINBERG and L. E. GLENDENIN, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, pp. 3–14. United Nations (1956).
[17] W. E. GRUMMITT and G. M. MILTON, *J. Inorg. Nucl. Chem.* **5**, 93 (1957).

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 206 to 222. Pergamon Press Ltd. Printed in Northern Ireland

# SHORT-LIVED BROMINE AND SELENIUM NUCLIDES FROM FISSION*†

J. E. SATTIZAHN, J. D. KNIGHT and M. KAHN‡
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

(*Received* 17 *February* 1959)

**Abstract**—A 6·0 ± 0·2 min bromine activity has been found in fission products and in rubidium bombarded with D-T neutrons. Experiments with enriched $^{85}$Rb and $^{87}$Rb support its assignment as an isomer of $^{84}$Br. $\beta$- and $\gamma$-scintillation counting with 100-channel pulse analysis indicate $\beta$ groups of 0·8 ± 0·1 MeV (20 per cent), 1·9 ± 0·2 MeV (72 per cent), and possibly 3·2 MeV (~8 per cent), plus prominent $\gamma$ rays of 0·44 ± 0·01 MeV (68 per cent), 0·88 ± 0·01 MeV (75 per cent), 1·46 ± 0·02 MeV (75 per cent), and 1·89 ± 0·03 MeV (16 per cent). The $^{235}$U thermal fission yields of the 6·0 min $^{84}$Br and the 31·7 min $^{84}$Br are (0·019 ± 0·003) per cent and (0·92 ± 0·06) per cent, respectively. By rapid separation of selenium from fission products and subsequent milking of the bromine daughters the half-lives of $^{85}$Se and $^{83}$Se have been measured as 3·3 ± 0·2 min and 39 ± 4 sec, respectively. The 6·0 min $^{84}$Br does not appear to grow from selenium. The experiments also produced evidence for a 16 ± 3 sec selenium parent of a 1·0 min bromine activity which is probably $^{87}$Br.

THE short-lived fission-product isotopes of bromine have recently received considerable attention because of their identification as delayed-neutron precursors. By rapidly sweeping bromine gas out of fission-product solutions, PERLOW and STEHNEY[1,2] isolated and measured delayed-neutron activities of half-lives 54 sec, 15·5 sec, 4·2 sec and 1·4 sec. The 54 sec period had been shown previously by SUGARMAN[3] to belong to $^{87}$Br. The 15·5 sec period appears to be identical with a 15·5 sec bromine found by SUGARMAN[3] and assigned as $^{88}$Br on the basis of rubidium milking experiments. The 4·2 sec period is evidently identical with the 4·51 sec delayed-neutron activity also observed by SUGARMAN[3,4] and provisionally assigned to $^{89}$Br.

The decrease in half-life with increase in mass number of the bromine delayed-neutron precursors prompted PERLOW and STEHNEY tentatively to assign the 1·4 sec period to $^{90}$Br.

The lighter fission-product bromines $^{83}$Br, $^{84}$Br, and $^{85}$Br were identified in early fission investigations. The decay of the 32 min $^{84}$Br was recently studied in detail by JOHNSON and O'KELLEY.[5]

This series of bromine isotopes reveals two features of radiochemical interest:

(1) the apparent absence of $^{86}$Br, which on the basis of simple mass number-decay period considerations might be expected to have a half-life of the order of one minute, and

(2) the apparent discrepancy in the fission yields reported for $^{84}$Br and for $^{84}$Kr.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

† This paper is a portion of the dissertation presented to the University of New Mexico by J. E. SATTIZAHN in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1957.

‡ University of New Mexico.

[1] G. J. PERLOW and A. F. STEHNEY, *Phys. Rev.* **107**, 776 (1957).
[2] G. J. PERLOW and A. F. STEHNEY, *Bull. Amer. Phys. Soc.* Ser. II, **3**, 1 (1958).
[3] N. SUGARMAN, *J. Chem. Phys.* **17**, 11 (1949).
[4] N. SUGARMAN, *J. Chem. Phys.* **15**, 544 (1947).
[5] N. R. JOHNSON and G. D. O'KELLEY, *Phys. Rev.* **108**, 82 (1957).

By mass-spectrometric measurement of krypton extracted from $^{235}U$ fission-product solutions, BLADES *et al.*[6] found a fission yield of 1·02 ± 0·05 per cent for stable $^{84}Kr$. On the other hand, KATCOFF *et al.*[7] reported a $^{235}U$ fission yield of 0·69 per cent for $^{84}Br$. From considerations of charge distribution in fission, it was evident that the difference in yields could not be attributed to independent formation of $^{84}Kr$. It appeared that a more plausible explanation, apart from experimental uncertainties, might be the existence of a hitherto undiscovered isomer of $^{84}Br$ through which a portion of the mass 84 chain could decay undetected. The possibility of isomerism is consistent with the low-energy states of $^{84}Br$ predicted by the nuclear shell model. These states, as derived by application of NORDHEIM's rule[8] to the combination of the odd-neutron orbitals $p_{1/2}$ and $g_{9/2}$ with the odd proton orbitals $f_{5/2}$ and $p_{3/2}$, are $1+$, $2-$, $\leq 3+$, and $\leq 6-$. JOHNSON and O'KELLEY[5] conclude that the most plausible assignment for the 32 min $^{84}Br$ is $2-$. Of the remaining states the $\leq 6-$ state offers a possibility of isomerism. Decay of such a state by $\beta$-emission would produce $^{84}Kr$ without a corresponding production of 32 min $^{84}Br$.

Similar considerations may be applied to the prediction of the possible behavior of $^{86}Br$. Its lowest-lying states are expected to be $0-$ and $\leq 4-$, and at slightly higher energies, $2-$ and $\leq 6-$. Because all four of these states have odd parity, whereas the ground state of the daughter $^{86}Kr$ is almost certainly $0+$ and the first excited state is most likely $2+$, the $\beta$-decay of $^{86}Br$ to the first two levels of $^{86}Kr$ must be at least first forbidden. The total $\beta$-decay energy of $^{86}Br$ should be approximately 8 MeV. With the ground state of $^{86}Br$ taken as $0-$ and with reasonable assumptions concerning the low-energy level structure of $^{86}Kr$, one may estimate that the half-life of $^{86}Br$ is about 30 sec. The choice of any of the remaining spin and parity possibilities for the ground state of $^{86}Br$ would lead to a longer half-life.

Of the selenium parents of the fission-product bomines, only $^{81}Se$ and $^{83}Se$ have been well characterized. The half-life of $^{84}Se$ has been reported by Manhattan Project workers[9] as approximately 2 min, but neither experimental details nor data are given. No information has been reported on selenium isotopes of mass >84.

The present investigation had as its primary aim a radiochemical exploration of the bromine activities of masses 84 and 86 and of the selenium activities of masses ≥84.

## EXPERIMENTAL

*Irradiation facilities.* The fission-product source material was obtained by irradiation of 93% $^{235}U$ (as the metal, wrapped in aluminium foil, or as the nitrate) in the Los Alamos Water Boiler. The capsules containing the uranium samples were inserted in the reactor by a pneumatic transfer device; for very rapid work they could be propelled through a tube directly into the chemical laboratory. The high-energy neutrons used in parts of this investigation were produced by the $^{3}H(d,n)^{4}He$ reaction in a Cockcroft-Walton accelerator.

*Radiation measurements.* $\beta$-counting for decay measurements was carried out with methane-flow proportional counters with 4·8 mg/cm² aluminium windows, 2 in. in diameter. The dead-time loss was approximately 1 per cent at $10^{3}$ counts/min. $\beta$- and $\gamma$-spectrum measurements were performed with a conventional scintillation apparatus, in conjunction with a Los Alamos Model II 100-channel

[6] A. T. BLADES, W. H. FLEMING and H. G. THODE, *Canad. J. Chem.* **34**, 233 (1956).
[7] S. KATCOFF, B. FINKLE and N. SUGARMAN, *Radiochemical Studies: The Fission Products*, (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Part V, Div. IV, Vol. 9, p. 587. McGraw-Hill, New York (1951). This series reference will be abbreviated hereafter as NNES-PPR (division, volume).
[8] L. A. NORDHEIM, *Rev. Mod. Phys.* **23**, 322 (1951).
[9] Editors' Note, NNES-PPR, Part V, Div. IV, Vol. 9, p. 587. McGraw-Hill, New York (1951).

pulse-height analyser. The $\beta$-scintillator consisted of a $\frac{5}{8}$ in. thick by $1\frac{9}{16}$ in. diameter trans-stilbene crystal packed in $Al_2O_3$ and covered with 0·2 mil aluminium foil. The major part of the $\gamma$-analysis was done with $1\frac{1}{2}$ in. $\times$ $1\frac{1}{2}$ in. and 2 in. $\times$ 2 in. NaI(Tl) scintillators.

The computations required for the analysis of $\beta$-spectrum data and for least-squares evaluation of decay data were performed with an IBM Electronic Data Processing Machine, Type 704.

*Chemical procedures*

I. *Quantitative separation of bromine from fission products.* The procedure was essentially that of GLENDENIN *et al.*[10] as modified by RAMANIAH.[11] The irradiated uranium metal, wrapped in aluminium foil, was dissolved in 6FHCl which contained a known quantity of bromide carrier. The bromide was oxidized to bromine with cerium (IV), extracted into $CCl_4$, and then re-extracted with aqueous $NaHSO_3$. After acidification of the aqueous bromide solution with $HNO_3$, iodine activity was removed by oxidation of added iodide carrier to iodine with excess $NaNO_2$ and subsequent extraction into $CCl_4$. Finally, the bromide was oxidized to bromine with excess $KMnO_4$, extracted into $CCl_4$, and re-extracted into aqueous $NaHSO_3$; this solution was acidified and boiled to expel $SO_2$. Silver bromide was precipitated and prepared for counting.

II. *Rapid qualitative separation of bromine from fission products.* This separation was performed by the method of STRASSMANN and HAHN.[12] Irradiated $UO_2(NO_3)_2 \cdot 6H_2O$ was placed in a distillation flask containing bromide carrier and $3FH_2SO_4$. The bromide carrier was oxidized to bromine with an equivalent amount of $NaBrO_3$, and the evolved bromine was swept by nitrogen gas into a solution containing $FeSO_4$ and iodide carrier. The iodide was oxidized to iodine with $NaNO_2$ and extracted into $CCl_4$, and the bromide was precipitated as AgBr and prepared for counting.

STEHNEY and SUGARMAN[13] had shown that a 20 sec distillation of this kind carried over less than 1 per cent of the iodine activity in the flask. The procedure was tested for the present work by carrying out a 15 sec distillation on a one-week-old fission-product solution representing $10^{12}$ fissions. After one week of decay the dominant fission-product halogen activities are 8 day $^{131}I$ and 2·4 hr $^{132}I$ which is in equilibrium with 77 hr $^{132}Te$. Within experimental error, no activity was observed in the final AgBr precipitate.

III. *Rapid quantitative separation of bromine from fission products.* Irradiated uranium metal was placed in a distillation flask containing a known quantity of bromide carrier in hot 3FHCl. After the uranium had dissolved (about 2 min), the bromine was oxidized to bromine with cerium (IV), and the evolved gas was swept into a receiving vessel. The bromine was then isolated as in Procedure II. The final AgBr precipitate was washed with saturated $(NH_4)_2CO_3$ to remove any AgCl resulting from free chlorine carried over during the bromine distillation. After the counting was completed, the sample was removed from its mount and the AgBr yield was determined.

IV. *Separation of selenium from fission products.* This procedure, which was adapted from the method of EDWARDS *et al.*[14] is based on the adsorption of radioselenium on freshly-formed selenium metal. Fifteen minutes before it was to be used, a suspension of selenium metal was prepared by reducing selenite carrier in conc. HCl with $SO_2$. Tellurite carrier was added as a hold-back carrier for fission-product tellurium. The irradiated $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved in the suspension and stirred for 30 sec. The selenium was filtered off with a coarse sintered-glass filter funnel, washed with conc. HCl and water, and dissolved in hot conc. $HNO_3$. The resulting selenite solution, diluted to $3FHNO_3$, was the parent solution from which the bromine activities were milked.

V. *Separation of bromine grown from selenium.* Bromine activity was milked from its selenium parent by either of two methods: extraction into $CCl_4$ or adsorption on freshly-formed AgBr. The $CCl_4$ extraction was regarded as being more reliable, but the time required for separation of the organic and aqueous phases limited its application to selenium half-lives greater than about 1 min. The AgBr adsorption method, developed for the determination of selenium half-lives as short as 15 sec, was based on the observation that freshly-precipitated AgBr exchanges rapidly with bromide ion[15]

[10] L. E. GLENDENIN, R. R. EDWARDS and H. GEST, NNES-PPR, Part VI, Div. IV, Vol. 9, p. 1451. McGraw-Hill, New York (1951).
[11] M. V. RAMANIAH. Thesis, Washington University, St. Louis, Mo. (1956).
[12] F. STRASSMANN and O. HAHN, *Naturwissenschaften* **28**, 817 (1940).
[13] A. F. STEHNEY and N. SUGARMAN, *Phys. Rev.* **89**, 194 (1953).
[14] R. R. EDWARDS, H. GEST and T. H. DAVIES, NNES-PPR, Part II, Div. IV, Vol. 9, p. 237. McGraw-Hill, New York (1951).
[15] I. M. KOLTHOFF and A. S. O'BRIEN, *J. Amer. Chem. Soc.* **61**, 3409, 3414 (1939).

Vol. 12 1959/6

and with hypobromite[16] at low concentrations, and thus that a AgBr precipitate, when mixed with a radioactive selenite solution for a few seconds, would effectively remove all the radiobromine.

EDWARDS *et al.*,[14] studying the chemical state of radiobromine grown from selenium parent contained in carrier selenite ion, found that about 50 per cent of the bromine existed as bromate at pH 8. ADAMS and GILBERTSON[17] found that bromate is readily reduced by selenite in the presence of small amounts of $HNO_2$. In the present experiments the growth was allowed to proceed in $\sim 3FHNO_2$; under these conditions the bromine should have existed as bromide ion.

In the $CCl_4$ extraction method, the selenite solution obtained from Procedure IV was added to a solution of bromine in $CCl_4$, and the mixture was shaken for a fixed time. The time at which the shaking was stopped was recorded by stopwatch, and the mixture was allowed to stand 30 sec for separation of the layers. The first $CCl_4$ layer was discarded; thereafter, successive portions of the bromine-$CCl_4$ solution were added, shaken, and drained off. To each of the $CCl_4$ portions was added a solution of iodide carrier in $1FHNO_2$, followed by a solution of $NaNO_2$ to oxidize the iodide to iodine and to reduce the bromine to bromide. The mixture was shaken and separated and the aqueous layer was shaken with $CCl_4$. The aqueous layer was again separated and the bromine was precipitated as AgBr, weighed, and mounted for counting. The procedure was tested on $^{83}$Se (25 min), which is known to decay to $^{83}$Br (2·3 hr). Six successive milkings of the bromine activity were performed at 10 min intervals. The observed half-life for $^{83}$Se of 24·8 min agreed with the accepted value of $25 \pm 1$ min.

In the AgBr adsorption method, the adsorbing precipitates were freshly prepared, usually within a half hour of their use. After the separation of the radioselenium by Procedure IV, the selenium metal was dissolved in 4 ml of hot conc. $HNO_2$ and added to a 40 ml centrifuge tube containing the freshly precipitated AgBr in 16 ml of $0{\cdot}4FHNO_3$. The suspension was stirred for 1 min or less, depending on the half-life under investigation, and the AgBr was then filtered out on a No. 41 Whatman filter mounted on a ground-off Hirsch funnel surmounted by a glass chimney. The filter funnel was mounted on a micro bell jar provided with a suction fitting and containing a 100 ml beaker to catch the filtrate. After the liquid had been drawn through the filter, the bell jar was quickly removed, and the contents of the beaker were poured into a second centrifuge tube containing fresh AgBr covered with 1 ml of $6FHNO_3$. These cycles, each with its own adsorption and filtration step, were repeated at carefully-timed intervals as often as necessary. Zero time was arbitrarily chosen as that time when the AgBr suspension was filtered. After removal of the active filtrate, each AgBr precipitate was washed, dried with acetone, and mounted for counting. Since the bromine activity was not uniformly distributed in the AgBr, the amount of AgBr recovered could not be taken as a measure of the radiochemical yield.

The AgBr adsorption procedure was tested on fission-product $^{83}$Se. A series of six successive AgBr extractions was performed at 25 min intervals, and the AgBr was recovered as completely as possible and counted. The half-life of $^{83}$Se as derived from the 2·3 hr decay component in the AgBr samples was $23 \pm 1$ min. The decay of the AgBr samples showed evidence of contamination by iodine activity which was assumed to have originated from decay of small amounts of fission-product tellurium adsorbed on the pre-formed selenium metal. In experiments involving the growth and measurement of the 32 min $^{84}$Br, the contribution of the iodine contamination (principally 52 min $^{134}$I) was minimized by $\beta$ counting through 444 mg/cm$^2$ of aluminium. In the experiments concerned with the extraction and measurement of $^{87}$Br, however, the iodine contaminants in the same half-life range could not be eliminated with assurance by counting methods alone. Accordingly, a short purification step was inserted prior to the selenium adsorption step. Immediately after removal from the reactor, the irradiated $UO_2(NO_3)_2{\cdot}6H_2O$ was dissolved in hot 3FHCl and passed rapidly through a column of AG 1-X8, 50–100 mesh anion resin. Separate experiments with solutions containing milligram quantities of selenite and tellurite ion had shown that under these conditions the selenite ion passed through, while practically all the tellurite ion remained on the column. When the $^{83}$Se–$^{83}$Br extraction experiment was repeated with inclusion of the anion-resin column step, it was found that less than 0·5 per cent of the possible iodine activity appeared in the final AgBr precipitate.

VI. *Separation of radiobromine from rubidium nitrate.* When radiobromine is formed by a $^{87}$Rb$(n,\alpha)^{84}$Br reaction, the probable contaminants are $^{84}$Rb and $^{86}$Rb, produced by the $(n,2n)$ reaction

[16] R. R. EDWARDS and H. GEST, NNES-PPR, Part VI, Div. IV, Vol. 9, p. 1454. McGraw-Hill, New York (1951).
[17] D. F. ADAMS and L. I. GILBERTSON, *Analyt. Chem.* **14**, 926 (1942).

on $^{85}$Rb and $^{87}$Rb, and $^{83}$Kr and $^{87}$Kr, produced by the $(n,p)$ reaction on $^{85}$Rb and $^{87}$Rb. Two methods were used to separate the bromine activities:

(1) the $RbNO_3$ was dissolved in 0·1F$HNO_3$ containing bromide carrier, and AgBr was precipitated with $AgNO_3$;

(2) the $RbNO_3$ was dissolved in 3F$HNO_3$, and a solution of $CCl_4$ containing bromine carrier was added. The layers were mixed by shaking, and the $CCl_4$ containing the radiobromine was separated. The bromine was then extracted into an aqueous solution of $H_2SO_3$ as bromide. Silver bromide was then precipitated by adding $AgNO_3$.

## EXPERIMENTAL RESULTS

### *Discovery of the* 6 min *isomer of* $^{84}$Br

The first set of experiments was carried out to explore the fission-product bromine activities of half-life $\geq$3 min. The known activities which fall within this category are 2·3 hr $^{82}$Br, 32 min $^{84}$Br and 3·0 min $^{85}$Br. Of these three nuclides and their descendants only the $^{84}$Br emits any significant amount of $\gamma$-radiation. The 4·4 hr $^{85m}$Kr emits a 0·150 MeV $\gamma$-ray in its $\beta$-decay branch and, at considerable lower intensity, a 0·300 MeV $\gamma$-ray in its isomeric transition branch; however, its half-life is sufficiently long to permit the determination of its contribution to the total bromine activity.

Because the $\gamma$-ray spectrum of the bromine samples at the longer times after irradiation was expected to be predominately that of the 32 min $^{84}$Br, its half-life and $\gamma$-spectrum were remeasured. For the half-life measurement, two portions of $^{235}$U were irradiated in the reactor, the bromine was separated by Procedure I, and the AgBr samples were counted through 444 mg/cm$^2$ of aluminium absorber with the standard methane-flow $\beta$-proportional counters. Plots of the decay indicated that from approximately 35,000 counts/min down to background only one component was present. The half-life as determined from a least-square analysis of the data was 31·7 min with a standard deviation of 0·2 min. For all work thereafter, the half-life of $^{84}$Br was taken as 31·7 min. The $\gamma$-spectrum measurement and a test of the validity of the distillation method for isolating pure bromine activity were combined in a second experiment. A sample of $UO_2(NO_3)_2 \cdot 6H_2O$ enriched in $^{235}$U was irradiated in the reactor for 3 min, and the radioactive bromine was separated by Procedure II. A series of 13 successive $\gamma$-spectrum measurements was made at approximately 5 min intervals starting 30 min after the end of irradiation. Plots of the logarithms of the counting rates vs. channel number for the family of spectra showed that the $\gamma$-ray spectrum of the active bromine above 0·6 MeV remained constant in shape over the time span covered.

The search for shorter-lived fission-product bromine activities was begun with a third experiment, similar in technique to the second but conducted on a shorter time scale. A sample of the $^{235}$U salt was irradiated in the reactor for 10 sec, and the radioactive bromine was separated by Procedure II. The distillation of bromine was started 49 sec after the end of irradiation and was continued for 15 sec. The first $\gamma$-spectrum measurement was started 11 min after the end of irradiation, and a series of 3 min counts (with an additional 2 min required for print-out of data) was taken. Examination of the spectra revealed a component of half-life shorter than 31·7 min. This component was most conspicuous in the 0·9 and the 1·5 MeV photopeaks. Decay plots of the total counts represented by each peak could be resolved clearly into components of half-life about 32 min and 6 min. Similar plots of the decay of other

Vol. 12 1959/6

portions of the $\gamma$-scintillation spectra exhibited short-lived and long-lived components. The spectrum of the short-lived component was obtained by subtraction of the 31·7 min component from the first spectrum observed. The spectra of both components are shown in Fig. 1. The similarity of portions of the two spectra, particularly the photopeaks at 0·9 and 1·5 MeV, suggested that the new activity might represent an isomer of $^{84}$Br.

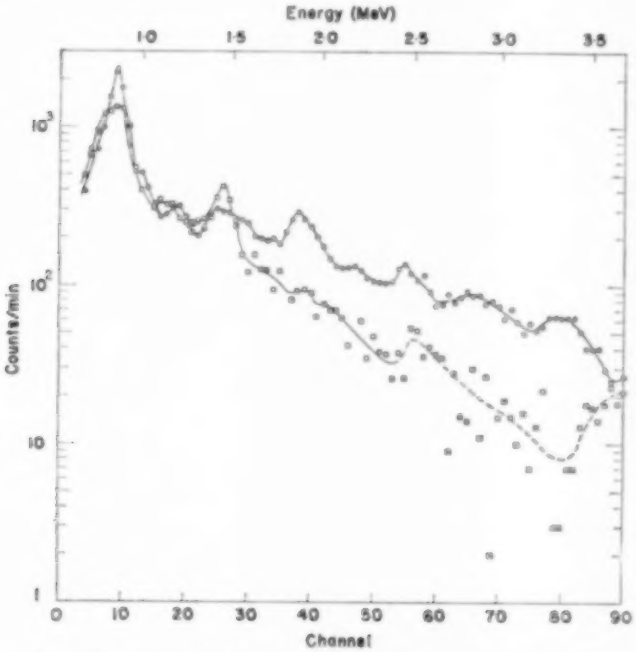



FIG. 1.—Scintillation $\gamma$-spectra of 6 min and 32 min components in fission-product bromine. 2 in. × 2 in. NaI(Tl) crystal.
○ 32 min component;
□ 6 min component.

The identity and some of the properties of the postulated isomeric state were established by examination of the bromine activity produced by irradiation of rubidium with D-T neutrons. Samples of $RbNO_3$ varying in isotopic abundance were exposed for periods of 2–6 min to D-T neutron fluxes of $\sim 3 \times 10^{10}$ n/cm$^2$ sec at a Cockcroft–Walton accelerator. In the initial irradiations, carried out to determine whether or not the 6 min bromine activity could be produced from rubidium, samples of normal (27·8% $^{87}$Rb) rubidium and enriched rubidium (89·62% $^{87}$Rb)* were exposed for 5 min, and the bromine activity was separated by the AgBr adsorption method (Procedure VI). The $\beta$-decay of both AgBr samples exhibited 6 min, 31·7 min, and 35·9 hr components. The decay data from the enriched $^{87}$Rb run are plotted in Fig. 2. The half-life of the shorter component, as determined by least-squares analysis, was 6·08 ± 0·12 min. Comparison of the bromine activities from the two samples indicated that both the 6 min period and the 31·7 min period were associated with $^{87}$Rb.

* The enriched isotopes were obtained from the Stable Isotopes Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

This result was confirmed by further experiments with highly enriched rubidium (95·9% $^{87}$Rb) and depleted rubidium (0·9% $^{87}$Rb). The bromine from the depleted sample was precipitated directly as AgBr and was $\beta$-counted. The bromine from the highly enriched sample was isolated by the $CCl_4$ extraction (Procedure VI) and was divided into two portions; the first portion was $\beta$-counted, and the second was used for the $\gamma$ spectrum analysis described in a later part of this section. The relative sizes of the two portions were determined by $\beta$-counts of their 31·7 min components. The

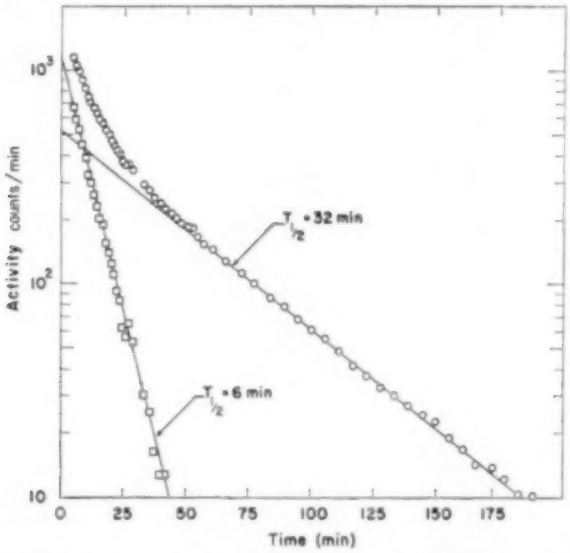



FIG. 2.—$\beta$-decay of bromine from D-T neutron irradiation of enriched $^{87}$Rb.

$\beta$-decay data of the first portion, together with its absolute counting efficiency (computed later on the basis of the $\beta$-energy spectrum of the 6·0 min component) and the measured activity ratio, were used to compute the $\beta$-disintegration rate of the 6·0 min component in the $\gamma$-spectrum portion. Least-squares analysis of the $\beta$-decay data gave a half-life of 5·91 $\pm$ 0·20 min for the shortest component. From an average of this value and the corresponding value obtained from the irradiation represented in Fig. 2, with allowance for possible sources of systematic error, the half-life of the short component was determined to be 6·0 $\pm$ 0·2 min.

The results of the four irradiations, summarized in Table 1, show that:

(1) the ratio of the 6·0 min activity to the 31·7 min activity is essentially independent of the enrichment of the $^{87}$Rb;

(2) the 6·0 min activities are associated with $^{87}$Rb.

Because the only bromine-producing reactions expected from 14 MeV neutrons on rubidium are of the $(n,\alpha)$ type, it was concluded that the 6·0 min activity is an isomer of $^{84}$Br.

The $\gamma$-scintillation spectrum of the 6·0 min $^{84}$Br was observed with a 1½ in. × 1½ in. NaI(Tl) crystal. As with the measurements on the fission-product bromine, the $\gamma$-spectrum of the 6·0 min component was obtained by subtraction of the spectrum of the 31·7 min component from the gross spectrum observed at earlier times. The

Vol. 12 1959/6

$\gamma$-scintillation spectrum of the 6·0 min $^{84}$Br obtained in this manner is shown in Fig. 3. A series of six spectra, taken at approximately 5 min intervals and treated in the same manner, showed that the photo-peaks at 0·44, 0·88 and 1·46 MeV decayed with a 6 min half-life.

The $\beta$-scintillation spectrum of the 6·0 min isomer of $^{84}$Br was measured on a second source of $^{87}$Rb$(n,\alpha)$ origin. The source consisted of 8·4 mg/cm$^2$ of AgBr in a 0·5 cm diameter circle on filter paper mounted on cardboard and covered with 9 mg/cm$^2$ of Scotch tape. As with the $\gamma$-spectra, two sets of measurements, one of a

TABLE 1.—BROMINE ACTIVITIES PRODUCED BY D-T NEUTRONS ON RUBIDIUM

| $^{87}$Rb/$^{85}$Rb | Counts/min $^{84}$Br* | | Counts/min $^{82}$Br | $\frac{\text{6·0 min } ^{84}\text{Br}}{\text{31·7 min } ^{84}\text{Br}}$ | $\frac{\text{6·0 min } ^{84}\text{Br}}{\text{35·9 hr } ^{82}\text{Br}}$ |
|---|---|---|---|---|---|
| | 31·7 min | 6·0 min | | | |
| 23·4 | 11,600 | 34,250 | 10 ± 3 | 2·95 | 3400 |
| 8·63 | 5773 | 15,156 | 10 ± 3 | 2·63 | 1500 |
| 0·385 | 2743 | 8055 | 173 | 2·94 | 46 |
| 0·0091 | 325 | 1000 | 230 | ~3 | ~4 |

* Corrected for decay during irradiation.

composite of the 6·0 min and 31·7 min activities, and the other of the 31·7 min component were required. A Fermi–Kurie plot of the $\beta$-spectrum of the 6·0 min component, plotted in Fig. 4, could be resolved into groups of end-point energies 3·2 MeV (8 per cent), 1·9 MeV (72 per cent) and 0·8 MeV (20 per cent). Inasmuch as the $\beta$-spectrum above 1·9 MeV was mainly that of the 31·7 min $^{87}$Br, the intensity of the 3·2 MeV component may be in error by a factor of two. The observed radiations of the 6·0 min $^{84}$Br are summarized in Table 2. Because of the relatively low source intensities available, as well as the rapid decay of the isomeric $^{84}$Br, only the dominant $\gamma$-rays and $\beta$-ray groups could be measured. However, it is noteworthy that the three lowest-energy $\gamma$-rays occur in approximately equal intensities, which together with the intensity of the 1·9 MeV $\beta$-ray group, indicate that these three $\gamma$-rays represent a cascade to the $^{84}$Kr ground state from the level fed by $\beta$-decay of the 6·0 min $^{84}$Br. The sum of the four energies involved gives a $Q_\beta$ of 4·68 MeV, with a probable error of 0·30 MeV. The $Q_\beta$ for the 31·7 min $^{84}$Br has been given[5] as 4·71 MeV; the similarity in the $Q_\beta$ values and the rather large energy uncertainty assigned to the $Q_\beta$ of the short lived isomer do not permit a conclusion as to which is the upper state.

DUFFIELD and LANGER,[18] in an earlier investigation of the 31·7 min $^{84}$Br, looked for a short-lived isomeric daughter of this species. On the basis of a Szilard–Chalmers reaction, they concluded that such an isomer, if it exists, has a half-life less than 30 sec, or the $\gamma$-ray associated with the isomeric transition is not sufficiently converted to give a measurable separation of the isomers. Since the present work developed information which these investigators did not have, namely, the definite existence of a short-lived isomeric state, an experiment similar to theirs was repeated to ascertain

[18] R. B. DUFFIELD and L. M. LANGER, *Phys. Rev.* **81**, 203 (1951).

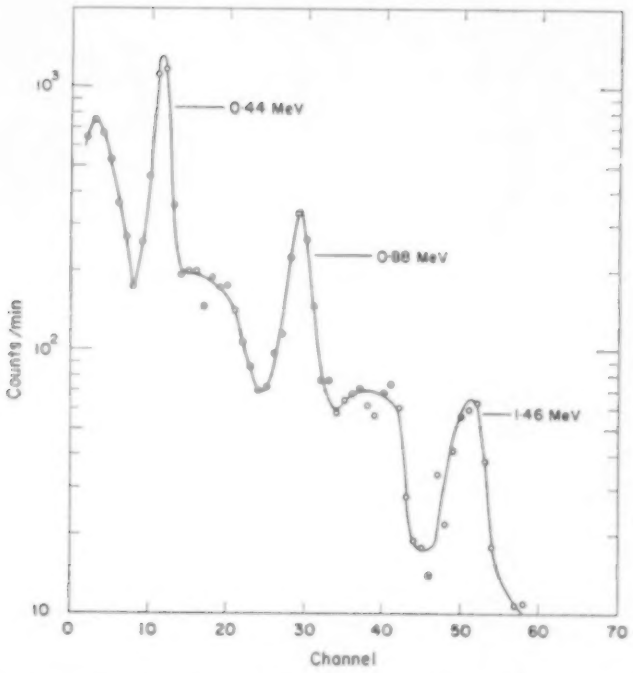



FIG. 3.—Scintillation $\gamma$-spectrum of 6 min $^{84}$Br produced by D-T neutron irradiation of $^{87}$Rb.

Vol. 12 1959/6

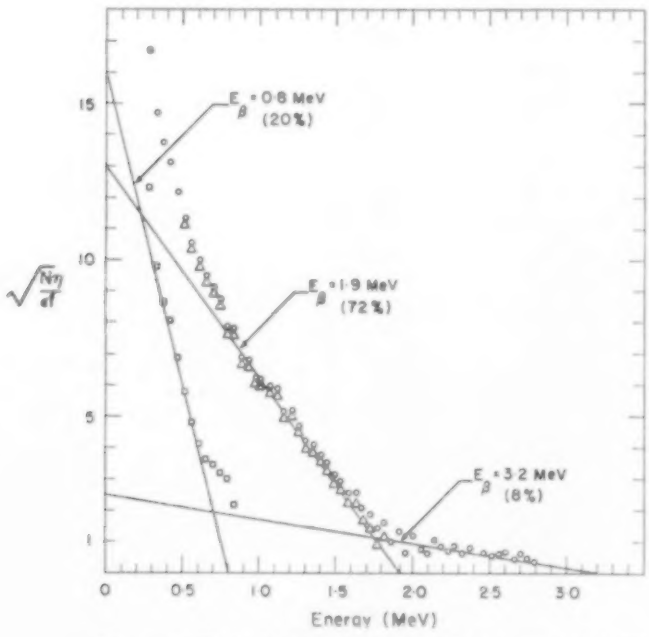



FIG. 4.—Fermi–Kurie plot of scintillation $\beta$-spectrum of 6 min $^{84}$Br.

whether the 6·0 min state was formed by isomeric transition from the 31·7 min state. A sample of 31·7 min $^{84}$Br, isolated from fission products, was incorporated in tribromophenol, and the latter was dissolved in benzene. This solution was shaken with four successive portions of an aqueous phase containing bromide carrier, and silver bromide was precipitated from each of the aqueous extracts. The counts of each of the precipitates corresponded to about $10^{-4}$ of the original 31·7 min $^{84}$Br

TABLE 2.—RADIATIONS OF 6·0 min $^{84}$Br

(a) Principal $\gamma$-rays

| Energy (MeV) | Relative intensity | $\gamma$-Rays per $\beta$-disintegration |
|---|---|---|
| 0·44 ± 0·01 | 91 | 0·68 |
| 0·88 ± 0·01 | 100 | 0·75 |
| 1·46 ± 0·02 | 100 | 0·75 |
| 1·89 ± 0·03 | 22 | 0·16 |

(b) $\beta$-Ray groups

| End-point energy (MeV) | Intensity (%) | log $ft$ |
|---|---|---|
| 0·8 ± 0·1 | 20 | 4·1 |
| 1·9 ± 0·2 | 72 | 5·0 |
| 3·2 | (8) | (6·8) |

activity, each decaying with a half-life of about 32 min. None of the samples showed any indication of a shorter-lived component. From these results and from a comparison of the $\gamma$-spectra of the 6·0 min and the 31·7 min isomeric states, it was concluded that the former is not produced by isomeric transition from the latter.

*Half-lives of* $^{84}$Se, $^{85}$Se *and* $^{87}$Se

The half-lives of $^{84}$Se and $^{85}$Se were determined by periodic extraction and measurement of the daughter 31·7 min and 3·0 min bromine activities which grow from fission-product selenium. In addition, the half-life of another fission-product selenium isotope, probably $^{87}$Se, was determined by measurement of the 56 sec bromine activity. Separate experiments were carried out for each of the selenium half-lives so that the growth periods could be optimized for the individual cases.

The half-life of $^{84}$Se was determined by two separate experiments differing in the technique by which bromine was extracted. In the first, a solution of the selenium activity, prepared by adsorption from fission products on freshly precipitated selenium, as described in Procedure IV, was shaken with six successive portions of $CCl_4$ containing free bromine carrier. The time intervals between successive extractions were 2·5 min, except for the first extraction, in which the growth interval was only 2·0 min. The bromine activity was precipitated as AgBr, and was $\beta$-counted through

444 mg/cm$^2$ of aluminium absorber for 5 hr. In the second experiment the bromine activity was milked from the selenium solution by the AgBr adsorption technique described in Procedure V. Seven AgBr extractions were performed at 2·0 min intervals, and the AgBr samples were recovered as completely as possible and counted. The data from both experiments are plotted in Fig. 5. The first point in the curve obtained by the $CCl_4$ extraction method has been adjusted for the difference in growth

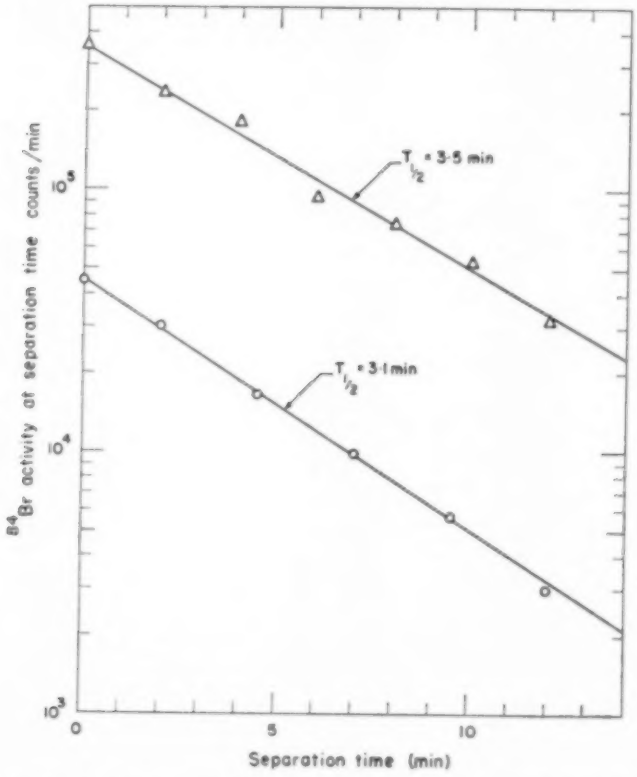



FIG. 5.—Decay of $^{84}$Se, computed from activities of $^{84}$Br extracted from fission-product selenium.
△ Extracted with silver bromide.
○ Extracted with carbon tetrachloride.

interval. These two determinations of the $^{84}$Se half-life, with allowance for possible sources of error, yielded an average value of 3·3 ± 0·3 min.

In the two experiments described above, the $\beta$-counting of the bromine samples was begun about 60 min after the bromine had been removed from the parent selenium solution. The decay of each sample showed only the 31·7 min component. The question of possible growth of the 6·0 min bromine from $^{84}$Se was treated in a separate pair of experiments in which the decay of bromine activity grown from fission product selenium was compared with the decay of bromine separated directly from fission products. In the first experiment a sample of enriched $UO_2(NO_3)_2 \cdot 6H_2O$ was irradiated for 3 min, and the separation and clean up of the fission product selenium

Vol. 12 1959/60

were completed 3 min after the end of irradiation. After the selenium had decayed an additional 3 min, the bromine activity was extracted from it by the $CCl_4$ method and $\gamma$-counted on a scintillation apparatus set to record $\gamma$-rays of energy $\geq 0{\cdot}5$ MeV. In the second experiment the $UO_2(NO_3)_2{\cdot}6H_2O$ was irradiated 30 sec, and the bromine separation was completed 95 sec after the end of irradiation. The $\gamma$-decay of the bromine milked from selenium had no detectable amount of a component with half-life shorter than 31·7 min. The $\gamma$-decay of the directly separated bromine, on the other hand, exhibited components of half-lives 31·7 min, ~5·5 min and ~1 min. The shortest period may be that of $^{87}$Br. These results lead to the conclusion that $^{84}$Se decays preponderantly to the 31·7 min isomer of $^{84}$Br, and that most of the 6·0 min $^{84}$Br is produced independently in fission.

The half-life of $^{85}$Se was determined by the same general method employed for $^{84}$Se, but the relatively short half-life (3·0 min) of the daughter $^{85}$Br necessitated the simultaneous use of separate $\beta$-counters for each of the bromine extracts. Three $\beta$-counters were employed, and thus three bromine extractions could be performed on a selenium preparation. The over-all $^{85}$Se decay curve was obtained from a series of similar milking experiments, the timing sequences of which were adjusted to provide an overlap in decay time, i.e. the first milking of the second sequence was completed at the same number of seconds after the end of irradiation as the third milking of the first sequence. The time available for manipulation in this experiment did not permit thorough recovery of the preformed AgBr precipitates, and the non-uniformity of adsorption of the active bromine on the precipitates precluded determination of radiochemical yield by the conventional weighing method. Instead, measurement of the activity of the 31·7 min $^{84}$Br, daughter of 3·3 min $^{84}$Se, was used to determine radiochemical yields. The $UO_2(NO_3)_2{\cdot}6H_2O$ was irradiated for 15 sec, the selenium was separated by Procedure IV, and the bromine activity was extracted from it by the AgBr method of Procedure V. In the first milking sequence the three bromine growth periods were 103–137 sec, 137–167 sec and 167–197 sec after end of irradiation; the growth periods for the second sequence were 167–197 sec, 197–227 sec and 227–257 sec. The timing of the individual AgBr separations was known to $\pm 3$ sec. The samples were $\beta$-counted through 272 mg/cm$^2$ of aluminium absorber, which had the effect of minimizing contributions from $^{83}$Br grown from $^{83}$Se. For the 6 hr span covered by the $\beta$-counts, the decay curves of the samples exhibited only 3 min and 32 min half-life components. The $^{85}$Se decay data derived from these $\beta$-counts are plotted in curve *A* of Fig. 6.

A source of concern in the above experiments was the possibility that the bromine from $\beta$-decay of selenium could occur in chemical species which do not exchange rapidly with the pre-formed AgBr adsorbent. A partial answer to this concern was sought in a second experiment in which the first milking sequence was carried out with hot solutions (~80°C) and the second with cold solutions (~5°C). The results, plotted together in Curve *B* of Fig. 6, show no indication of a temperature dependence.

As a rough check on the AgBr adsorption method, a milking experiment was carried out by the $CCl_4$ extraction procedure. Three milkings were conducted at 1 min intervals, representing about the limit of speed possible with this procedure. The results are plotted as Curve *C* of Fig. 6. The results embodied in all three curves of Fig. 6 are consistent with a $^{85}$Se half-life of $39 \pm 4$ sec.

In exploratory experiments involving the extraction of bromine from selenium

which had been separated very rapidly from fission products, the decay of the bromine had exhibited a prominent component of half-life about 1 min. The agreement of this half-life with the one reported for $^{87}$Br indicated that a measurable amount of $^{87}$Se had survived until the time of the bromine extraction. Accordingly, to determine the half-life of $^{87}$Se, four separate irradiations of uranyl nitrate were made, with only one bromine extraction performed in each case. Each of the irradiation times was

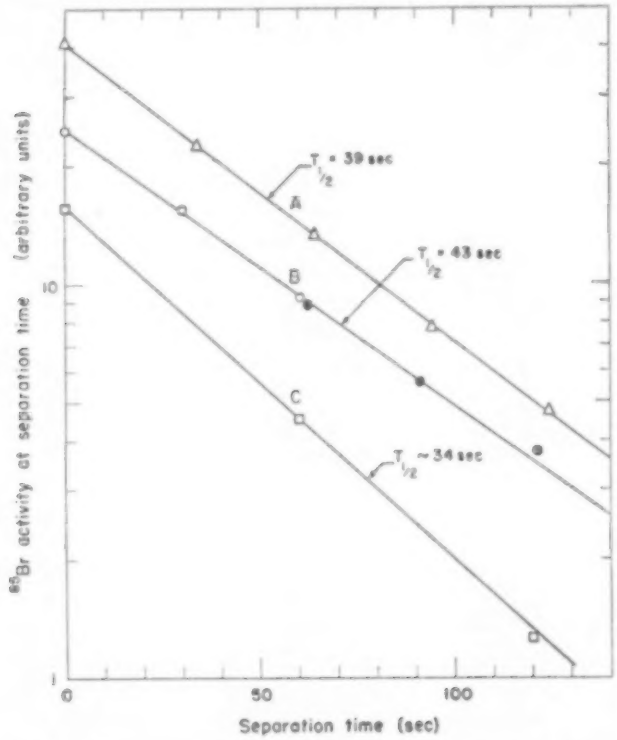



FIG. 6.—Decay of $^{85}$Se, computed from activities of $^{85}$Br extracted from fission-product selenium.
△ Extracted with silver bromide, room temp.
□ Extracted with silver bromide, 80°C.
● Extracted with silver bromide, 5°C.
□ Extracted with carbon tetrachloride.

$20 \pm 1$ sec, and the bromine growth intervals were 92–115 sec, 111–130 sec, 120–143 sec and 132–159 sec, all expressed in terms of time after end of irradiation.

The AgBr samples were $\beta$-counted through 1310 mg/cm$^2$ of aluminium absorber to permit the counting of only the relatively energetic $\beta$-particles of $^{87}$Br and $^{84}$Br. The bromine decay curves were resolved into 1 min and 31·7 min components, and as in the $^{85}$Se experiment, the 31·7 min component was used in conjunction with the previously measured $^{84}$Se half-life to normalize the 1 min components to a common radiochemical yield. A preliminary plot of the 1 min components without regard to the differences in growth period gave an apparent half-life of 15 sec for the selenium parent. The known half-life of $^{87}$Br (56 sec) and the approximate half-life of the

Vol. 12 1959/6

observed selenium parent were inserted in the parent-daughter expression

$$A_2(T_1 + t_1) = A_1(t_1)\ \frac{\lambda_2}{\lambda_2 - \lambda_1}\ [e^{-\lambda_1 T_1} - e^{-\lambda_2 T_1}]$$

and the relative values of $A_1(t_1)$ were again plotted as a function of $t_1$ (Fig. 7). The results, though considerably less certain than those of $^{85}$Se, indicate that the 1 min bromine activity grows from a selenium parent of half-life 16 ± 3 sec.

As a test of the internal consistency of the experiments that established the half-

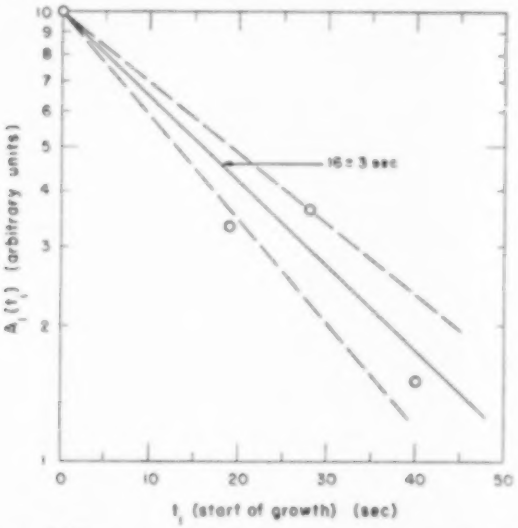



FIG. 7.—Decay of $^{87}$Se, computed from activities of $^{87}$Br extracted from fission-product selenium. Dashed lines indicate probable limits of error in half-life.

lives of $^{85}$Se and $^{87}$Se, the bromine decay data were used to compute the fission yields of $^{85}$Se and $^{87}$Se relative to the fission yield of $^{84}$Se. The computations for each experiment were carried out in a conventional manner:

(1) the decay components of the first bromine sample separated from the selenium were extrapolated back to the time of separation, i.e., the end of the first growth period, and the "zero time" $\beta$-counting rates so obtained were converted to absolute disintegration rates;

(2) from these disintegration rates and from the half-lives of the Se–Br Parent–daughter pairs, the disintegration rates of $^{84}$Se and of the other selenium isotope were computed as of the beginning of the growth period;

(3) these selenium disintegration rates, extrapolated to the end of the irradiation and corrected for decay during irradiation, gave the fission yield ratio $Y(^{A}\text{Se})/Y(^{84}\text{Se})$.

The ratio of the counting efficiency of $^{84}$Br with the various absorbers to the counting efficiency at zero absorber had been established by direct measurements. The corresponding ratios for $^{85}$Br and $^{87}$Br were estimated from various empirical data. The $\beta$-counting efficiencies for all three bromine isotopes at zero absorber were assumed to be identical. With the half-lives of $^{84}$Se and $^{85}$Se taken as 3·3 min and 39

sec, respectively, the fission yield ratio $Y(^{85}Se)/Y(^{84}Se)$ was 1·00 for the $CCl_4$ extraction method, 1·15 for the AgBr adsorption method, and 1·16 for the AgBr adsorption method from hot and cold solutions. The corresponding $^{85}Se$ fission yields, based on a yield of 0·98 per cent for $^{84}Se$, are 0·98, 1·13 and 1·14 per cent. These values are in agreement with a $^{85}Se$ fission yield of 1·12 per cent calculated by assuming that 84 per cent of the mass 85 chain (1·30 per cent)[19] is produced by predecessors of $^{85}Br$. With the half-life of $^{87}Se$ taken as 16 sec, the fission yield ratio $Y(^{87}Se)/Y(^{84}Se)$ was 2·06. The corresponding $^{87}Se$ fission yield is 2·02 per cent. The expected yield is estimated to be 1·37 per cent, based on the assumption that 56 per cent of the chain yield (2·44 per cent) is produced by predecessors of $^{87}Br$. This discrepancy does not appear unreasonably large in view of the uncertainty in the half-life of $^{87}Se$ and of the fact that the $^{87}Se$ activity was extrapolated about six half-lives from the beginning of the growth period back to the end of irradiation.

In the discussion thus far, the assumption has been made that the 1 min bromine activity observed was that of $^{87}Br$. However, in the light of estimates of the $\beta$-ray energy and probable half-life of $^{86}Br$, it is possible that the 1 min component observed in the bromine decays is the still-unidentified $^{86}Br$, and thus that the parent half-life measured is that of $^{86}Se$. The sources that could be handled by the present techniques were not strong enough to permit positive identification of $^{87}Br$ by neutron counting.

*Fission yields of the* 6·0 min *and* 31·7 min *isomers of* $^{84}Br$

The $^{235}U$ thermal neutron fission yields of the 31·7 min and 6·0 min isomers of $^{84}Br$ were measured in separate experiments. For each determination, a sample of uranium metal (93% $^{235}U$) wrapped in aluminium foil was irradiated at the edge of the sphere of uranium solution which constitutes the core of the water Boiler. After the uranium and its wrapper had been dissolved in HCl containing known weights of bromide and molybdenum carrier, the bromine was separated from solution, and the residue was set aside for $^{99}Mo$ analysis. The $^{99}Mo$ served as a monitor of the number of fissions in the sample. This 66·4 hr $\beta$-emitter (fission yield = 6·06 per cent) is the radiochemical fission reference standard used at this Laboratory, and the empirical ratio $K$ = fissions/$^{99}Mo$ activity is determined by radiochemical analysis of a $^{235}U$ sample in which the number of fissions has been determined by comparison fission counting.

In the measurement of the 31·7 min $^{84}Br$ (isolated by Procedure I), the purified bromide sample was $\beta$-counted through 444 mg/cm² of aluminium absorber to minimize the radiations from $^{83}Br$ and $^{83m}Kr$. The effect of the absorber on the counting efficiency of the $^{84}Br$ was determined separately by comparison of counting rates with and without absorber of a sample of the material produced by the $^{87}Rb(n,\alpha)^{84}Br$ reaction. The $\beta$-counting efficiency at zero absorber was calculated by reference to an empirically-determined calibration curve relating counting efficiency to average $\beta$-energy,[20] and was estimated to be accurate to $\pm 5$ per cent. The 31·7 min $^{84}Br$ activity was corrected for the finite length of the irradiation and for growth from a 3·3 min predecessor. The fission-yield values obtained from duplicate determinations were 0·905 and 0·927 per cent. With estimated uncertainties of 6 per

[19] J. A. PETRUSKA, H. T. THODE and R. H. TOMLINSON, *Canad. J. Phys.* **33**, 693 (1955): Summary of Canadian mass spectrometric data.
[20] B. P. BAYHURST and R. J. PRESTWOOD, *Nucleonics* **17**, No. 3, 82 (1959).

Vol. 12 1959/6

cent in the number of $^{84}$Br atoms and 3 per cent in the number of fissions, the fission yield was determined as (0·92 ± 0·06) per cent.

In the measurement of the 6·0 min $^{84}$Br, the irradiation time and the time to separation of the bromine were kept as short as possible to minimize the contribution of the 31·7 min isomer. Because of the contribution of the 3·0 min $^{85}$Br, together with the relatively low intensity of the 6·0 min $^{84}$Br, the latter could not be measured directly by $\beta$-counting. Instead, a series of $\gamma$-scintillation spectra was recorded and the area of the 0·44 MeV photopeak was taken as a measure of the 6·0 min activity. Then, the 0·44 MeV photopeak was calibrated in terms of disintegration rate by comparison of $\gamma$-spectrum and $\beta$-decay measurements on the 6·0 min component in a sample of bromine prepared by $^{87}$Rb$(n,\alpha)^{84}$Br. The fission-yield values obtained for duplicate determinations were 0·0190 and 0·0198 per cent. With estimated uncertainties of 15 per cent in the number of bromine atoms and 3 per cent in the number of fissions, the $^{235}$U fission yield of the 6·0 min isomer of $^{84}$Br was determined as (0·019 ± 0·003) per cent. The total fission yield of $^{84}$Br thus came out to be (0·94 ± 0·06) per cent. This value is in good agreement with the (1·02 ± 0·05) per cent fission yield reported for $^{84}$Kr.

*Search for shorter-lived activities*

A few preliminary experiments were undertaken in a search for new bromine activities of half-life 0·5–3 min. In these experiments, samples of uranyl nitrate were irradiated in the Water Boiler for 15 sec and the bromine activities were swept from the fission-product solution by Procedure II, and the mounted sources were observed with a $\gamma$-scintillation spectrometer. A series of spectra observed at times up to 8 min after the end of irradiation showed $\gamma$-rays of energies 1·42, 1·56, 2·0, 2·4, 2·7 and 3·2 MeV, the intensities of which decayed with a half-life $\leq$1 min. Of these $\gamma$-rays, only the two most prominent, at 1·42 and 1·56 MeV, were measured with sufficient accuracy to permit establishment of a definite decay rate. Their half-life of about 56 sec suggests that they belong to $^{87}$Br.

The question of the identification of $^{86}$Br remains unsolved. From the nuclear shell model considerations outlined in the introductory portion of this paper, and in particular from the fact that the 15·5 sec $^{88}$Br may be expected to have a shell structure similar to that of $^{86}$Br, a half-life of $<$0·5 min for the latter appears unlikely. On the other hand, the apparent absence of half-life components other than 1 min in the $\beta$-decay curves (from counts through 1310 mg/cm$^2$ of aluminium) of the bromine activities milked from short-lived selenium implies that if the half-life of $^{86}$Br is $\geq$0·5 min, the half-life of its selenium parent is $<$15 sec. The remaining possibility, that the half-life of $^{86}$Br lies in the range 50 to 60 sec and hence that the 1 min $\beta$-component observed consists of a composite of the decays of $^{87}$Br and $^{86}$Br, was not excluded in the present work. For this reason, the selenium parent of half-life 16 ± 3 sec may be $^{86}$Se or $^{87}$Se.

Although the identification of the 16 ± 3 sec selenium activity remains in doubt, its assignment to $^{87}$Se helps resolve a portion of the discrepancy between the fission yields reported for $^{87}$Br and $^{87}$Rb. The fission yield of $^{87}$Rb based on mass spectrometric measurements has been reported by Canadian investigators[19] as 2·49 per cent. On the other hand, the fission yield of $^{87}$Br was measured by STEHNEY and SUGARMAN,[13] who found a value of 3·13 per cent, referred to a $^{139}$Ba fission yield of

6·3 per cent; adjustment to the presently used fission yield of 6·55 per cent for $^{139}$Ba raises the $^{87}$Br value to 3·25 per cent. STEHNEY and SUGARMAN set an upper limit of ~13 sec for the half-life of the selenium precursor and used no $^{87}$Se–$^{87}$Br parent–daughter correction in their computations of the $^{87}$Br yield. However, the parent–daughter correction for a 16 sec selenium parent and a 56 sec bromine daughter lowers the computed yield by the factor 1·40 for that portion of the $^{87}$Br which grows from $^{87}$Se. If now 36 per cent of the mass 87 chain is assumed to be produced directly as $^{87}$Br and 56 per cent of the chain is produced as predecessors of $^{87}$Br, inclusion of the parent–daughter correction lowers the measured $^{87}$Br fission yield from 3·25 to 2·69 per cent. With the additional assumptions that 2 per cent of the $^{87}$Br decays are followed by delayed neutron emission, that 8 per cent of the mass 87 chain is produced directly as $^{87}$Kr, and that the chain yield is enhanced 4 per cent as a result of delayed-neutron emission following $\beta$-decay of $^{88}$Br, the fission yield of 2·49 per cent for $^{87}$Rb corresponds to a fission yield of 2·24 per cent for $^{87}$Br. The discrepancy between the 2·69 per cent value computed from direct measurement of the $^{87}$Br and the 2·24 per cent value computed from the $^{87}$Rb yield does not appear unreasonably large in view of the uncertainties in both the estimates and the measurements.

*Acknowledgement*—The authors wish to express their appreciation to Dr. J. H. COON and Mr. R. W. DAVIS for the Cockcroft-Walton irradiations and to Dr. M. E. BUNKER and Mr. J. W. STARNER and the staff of the Los Alamos Water Boiler for the thermal neutron irradiations. The authors are indebted to Dr. R. W. SPENCE and Dr. G. A. COWAN for their support and encouragement throughout the course of this work.

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1960, Vol. 13, pp. 223 to 227. Pergamon Press Ltd. Printed in Northern Ireland

# A NEW FISSION PRODUCT: $^{74}$Ga

J. A. MARINSKY* and E. EICHLER
Oak Ridge National Laboratory,† Oak Ridge, Tennessee

(*Received* 30 *April* 1959)

**Abstract**—The 8 min $^{74}$Ga has been separated from the fission products of $^{235}$U. This is believed to be the first observation of mass 74 in the fission process. The gallium activity was characterized as $^{74}$Ga by comparison of its $\gamma$-ray spectrum with that obtained from $(n,p)$-produced $^{74}$Ga.

Chemical separation of the $^{74}$Ga was effected by a combination of extraction, volatilization, ion-exchange, and precipitation steps. Its fission yield has been determined to be about $3{\cdot}4 \times 10^{-4}$ per cent, in good agreement with the yield expected for mass 74 from interpolation of the smooth mass-fission yield curve for $^{235}$U.

AN 8 min activity observed by bombarding natural germanium with fast neutrons was tentatively assigned to $^{74}$Ga by MORINAGA.[1] This assignment was confirmed by EICHLER *et al.*[2] through irradiation of enriched $^{74}$Ge with 14 MeV neutrons and through subsequent chemical separation. In addition, the yield of the 8 min activity was demonstrated to be proportional to the isotopic enrichment of $^{74}$Ge. The $\gamma$-ray spectrum of $^{74}$Ga is dominated by intense peaks at 0·60 and 2·3 MeV; weaker transitions with energies of 0·86, 1·1, 1·5 and 1·9 MeV are also observed. Since mass 74 had not yet been reported in fission, it was of interest in the present study to demonstrate the occurrence of the 8 min $^{74}$Ga activity in the fission process and to compare its yield with that predicted by the smooth mass-fission yield curve[3] for $^{235}$U. Sufficient knowledge of its half-life and $\gamma$-ray spectrum was available to aid in the identification. In addition, the availability of a multi-channel analyser provided rapid measurement capability.

## EXPERIMENTAL

### *Separation*

The separation procedure that was used in this study was a composite of standard techniques.[4,5,6,7] Each separate operation, however, was performed as rapidly as possible to minimize loss by decay of the 8 min gallium activity. As a result, optimum decontamination was sacrificed in some instances. For example, the ion exchange and precipitation steps would undoubtedly have provided more

* Permanent address: University of Buffalo, Buffalo, New York; Oak Ridge Institute of Nuclear Studies Research Participant, June–September 1958.

† Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

[1] H. MORINAGA, *Phys. Rev.* **103**, 504 (1956).
[2] E. EICHLER, N. R. JOHNSON and G. D. O'KELLEY, Abstract of a paper submitted at the New York meeting of the American Physical Society, January 29 to February 1 (1958); E. EICHLER, J. MARINSKY, N. R. JOHNSON and G. D. O'KELLEY. To be published.
[3] S. KATCOFF, *Nucleonics* **16**, 78–85 (1958).
[4] L. E. GLENDENIN, *Radiochemical Studies: The Fission Products*, (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, Book III, pp. 1657–1661. McGraw-Hill, New York (1951).
[5] J. M. SIEGEL and L. E. GLENDENIN, *Radiochemical Studies: The Fission Products*, (Edited by C. D. CORYELL and N. SUGARMAN) NNES Plutonium Project Record, Div. IV, Vol. 9, Book III, pp. 1436–1439. McGraw-Hill, New York (1951).
[6] G. E. LUNDELL and J. I. HOFFMAN, *Outlines of Methods of Chemical Analysis*. John Wiley, New York (1938).
[7] K. KRAUS and F. NELSON, *Metal Separations by Anion Exchange*. A.S.T.M. Symposium on Ion-Exchange and Chromatography in Analytical Chemistry, Atlantic City, New Jersey, June 18 (1956).

complete separation from the other fission products than was obtained if slower flow rates and longer digestion periods had been employed.

A 2 ml sample of uranyl nitrate solution (~850 mg U/ml) contained in a pneumatic transfer tube "rabbit" was irradiated for 2 min in the ORNL Graphite Reactor in a typical experiment. The micarta "rabbit" that was used is similar to that described by O'KELLEY *et al.*[8] except that it contained a stainless steel liner to hold the liquid sample. The "rabbit" was ejected from the reactor and dropped

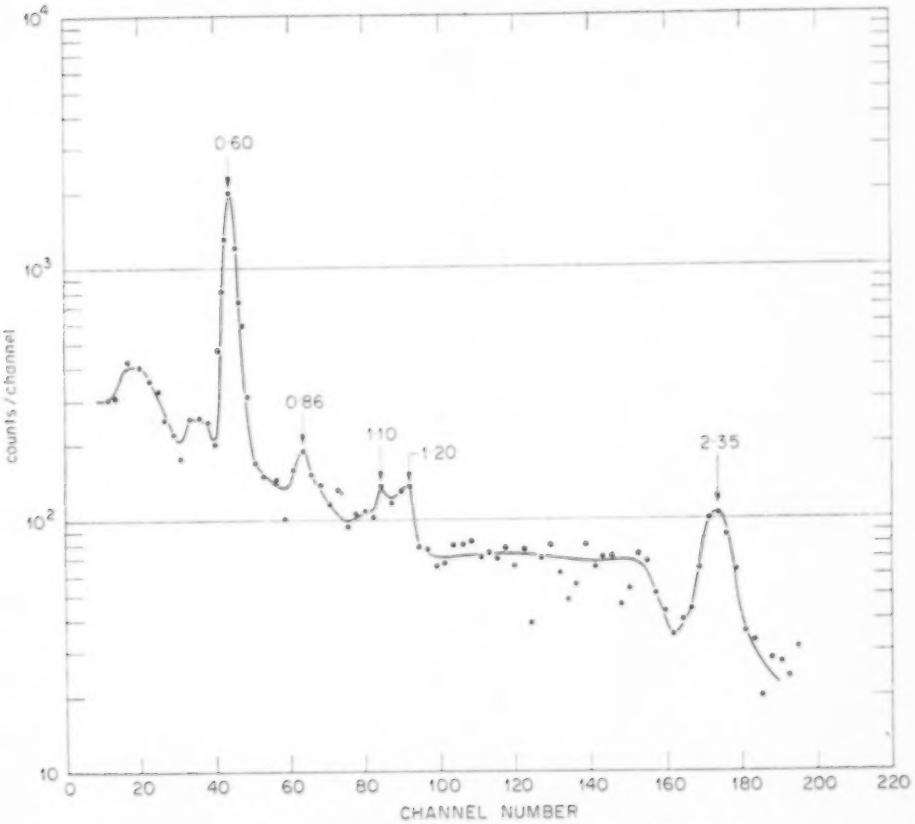



FIG. 1a.—The $\gamma$-ray spectrum produced by fission product gallium.

into a shielded holder for 2 min at the end of an irradiation to permit decay of the very short-lived nuclides. The liquid sample was then transferred pneumatically to a separatory funnel containing 2 ml of gallium carrier (~10 mg of Ga/ml), 2 ml of barium carrier (~10 mg of Ba/ml) and 6 ml of 12 M hydrochloric acid. The solution was then contacted with 12 ml of diisopropyl ether for 15 to 30 sec. The 12·8 day $^{140}$Ba was separated from aliquot samples of the aqueous phase to provide a fission-yield standard. The separation procedure of GLENDENIN,[4] which is based on the simple precipitation of $BaCl_2.2H_2O$, was used. The gallium was back extracted into 10 ml of water after washing the ether layer with three 5 ml portions of 6 M hydrochloric acid. This solution was made about 1 M in hydrofluoric acid and then was passed rapidly with compressed air through a Dowex-1 resin column to adsorb the molybdenum. The effluent was collected in 5 ml of concentrated hydrobromic acid.

The hydrobromic, hydrofluoric acid mixture was evaporated over an open flame. Excessive loss of gallium due to volatilization was avoided by evaporating the sample *just* to dryness. The residue

[8] G. D. O'KELLEY, N. H. LAZAR and E. EICHLER, *Phys. Rev.* **102**, 223 (1956).

was immediately dissolved in 10 ml of chilled 6 M hydrochloric acid and the gallium was extracted with 10 ml of cold diisopropyl ether. After washing the ether extract twice with 5 ml portions of 6 M hydrochloric acid, the gallium was back extracted once more into 10 ml of water. This aqueous sample was then made 0·3 M in hydrochloric acid after adding bismuth (~10 mg) and molybdenum (~3 mg) scavengers. After their precipitation with hydrogen sulphide and removal of the precipitate, additional molybdenum (3 mg) was precipitated with α-benzoinoxime. The filtrate

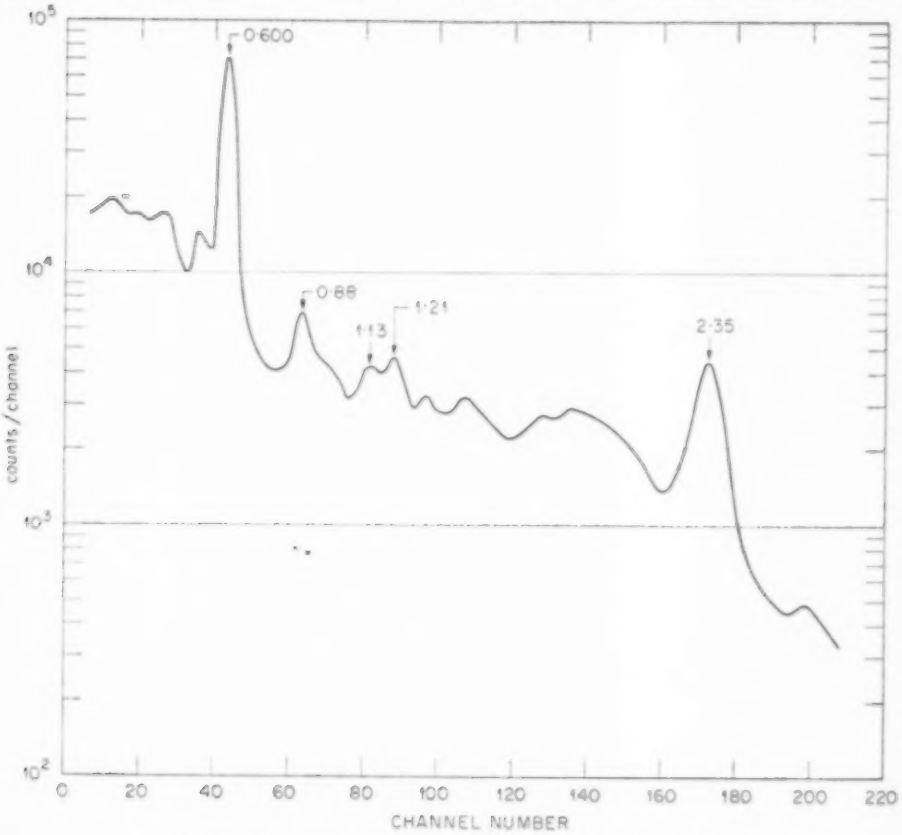



FIG. 1b.—The γ-ray spectrum produced by $^{74}$Ga from $^{74}$Ge$(n,p)$.

from the oxime precipitate was then made slightly basic with 6 M ammonium hydroxide and precipitated with 8-hydroxyquinoline reagent. The gallium 8-hydroxyquinolate precipitate was filtered on a weighed filter-paper disk and mounted for activity measurement.

*Nuclear measurement*

γ-ray spectra were measured with a 3 in. × 3 in. cylindrical sodium iodide crystal. Normally a 1·3 g/cm$^2$ polystyrene disk was placed between source and crystal to absorb β-radiation. Two types of spectral runs were performed:

(1) complete spectra were observed for comparison with the spectral shape obtained from $(n,p)$-produced $^{74}$Ga;

(2) the decay of the intense 0·60 MeV γ-ray was observed by measuring the low-energy portion of the spectra as a function of time.

The β-decay of $^{74}$Ga samples was followed with an end-window gas-flow proportional counter. For fission yield determinations, both the $^{74}$Ga and the $^{140}$Ba disintegration rates were obtained from γ-ray spectra. The $^{140}$Ba spectra were taken soon after separation to minimize $^{140}$La growth.

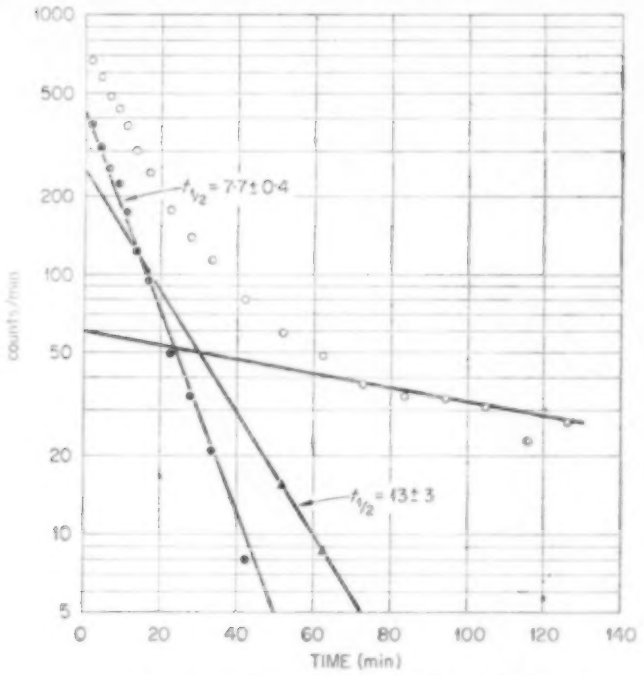



FIG. 2.—The $\beta$-decay of a fission product gallium sample.

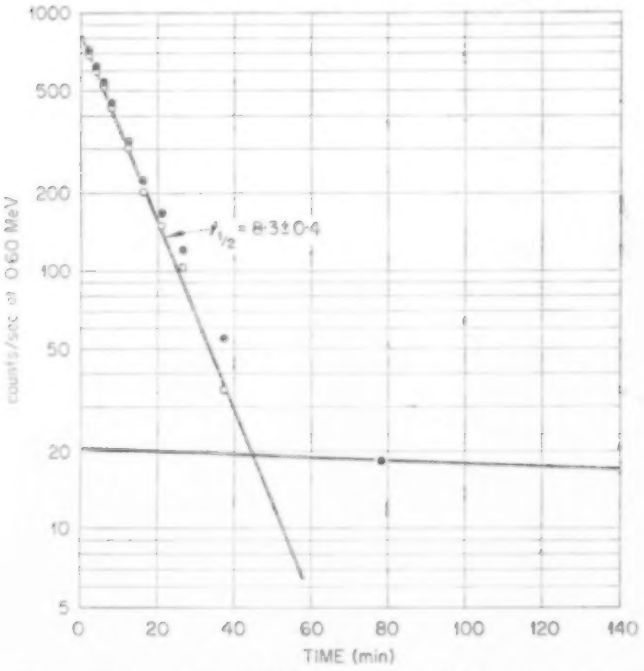



FIG. 3.—The decay of the 0·60 MeV $\gamma$-ray from a fission product gallium sample. The long-lived component was determined by an additional point at 270 min.

Vol.
12
1959/6

## RESULTS

### *Isotope identification*

The $\gamma$-ray spectrum produced by the gallium sample after separation from fission products is shown in Fig. 1a, while that produced by a sample of $^{74}$Ga resulting from $^{74}$Ge$(n,p)$ is given in Fig. 1b. The spectrum in Fig. 1a is a composite of two spectra: the portion below $\sim$0·80 MeV from a very pure but weak source, the portion above $\sim$0·80 MeV from a source with more activity but somewhat contaminated with $^{101}$Tc which has essentially no high energy $\gamma$-rays. It is seen that the fission product gallium produces a spectrum in good agreement with that from $^{74}$Ga.

TABLE 1.—RESULTS OF DETERMINATION OF FISSION YIELD OF $^{74}$Ga

| | Experiment | Bombardment time (min) | Time before counting (min) | Chemical yield | Corrected peak area | Absolute $\gamma$-ray intensity (%) | Fission yield (%) |
|---|---|---|---|---|---|---|---|
| $^{140}$Ba | 1 | 2·0 | 1670 | 0·360 | $1{\cdot}67 \times 10^7$ | 21·5[6] | 6·32[3] |
| | 2 | 2·3 | 4550 | 0·704 | $1{\cdot}88 \times 10^7$ | | |
| $^{74}$Ga | 1 | 2·0 | 31·2 | 0·395 | $3{\cdot}16 \times 10^5$ | 75[2] | $3{\cdot}42 \times 10^{-4}$ |
| | 2 | 2·3 | 33·5 | 0·475 | $3{\cdot}48 \times 10^5$ | | $3{\cdot}35 \times 10^{-4}$ |

[6] W. S. Lyon. Private Communication (August, 1958).

A $\beta$-decay study of the fission-produced $^{74}$Ga is shown in Fig. 2. The indicated half-life of 7·7 $\pm$ 0·4 min is in good agreement with the value of 7·8 $\pm$ 0·2 min previously assigned to this nuclide.[2] The extrapolated activity of the longest-lived component relative to that of 8 min $^{74}$Ga is of the magnitude to be expected from 5 hr $^{73}$Ga, produced in the fission process,[3] and the $\sim$13 min component probably is $^{101}$Mo-Tc. The decay of the 0·6 MeV $\gamma$-ray is shown in Fig. 3. An 8·3 $\pm$ 0·4 min half-life is resolved from this independent study.

### *Fission yield*

The area under the 0·60 MeV $\gamma$-ray peak of $^{74}$Ga and the 0·54 MeV $\gamma$-ray peak of $^{140}$Ba were corrected for decay, for degree of saturation during irradiation, for chemical yield, and for intrinsic peak efficiency. The fission yield of $^{74}$Ga was then calculated relative to the absolute fission yield of $^{140}$Ba using the respective absolute $\gamma$-ray intensities (the number of $\gamma$-rays per disintegration). Table 1 lists the data for two separate determinations. Averaging the two results gives a yield of $3{\cdot}4 \times 10^{-4}$ per cent with an expected error of 10–20 per cent; this is in good agreement with the value obtained by interpolation of the $^{235}$U mass-yield data.[3]

*Acknowledgements*—We would like to thank Drs. G. D. O'KELLEY, N. R. JOHNSON and G. E. BOYD for their assistance and encouragement.

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 228 to 233. Pergamon Press Ltd. Printed in Northern Ireland

# HALF-LIVES OF $^{149}$Pm AND $^{151}$Pm

L. R. BUNNEY, J. O. ABRIAM and E. M. SCADDEN
U.S. Naval Radiological Defense Laboratory, San Francisco 24, California

(*Received* 20 *April* 1959)

**Abstract**—New half-life values have been obtained for $^{149}$Pm and $^{151}$Pm. These radionuclides were produced by short concurrent neutron irradiations of enriched Nd isotopes and purified by ion exchange chromatography after the decay of the Nd parents. Counting conditions and instruments were selected to minimize the small mutual interferences of the two radionuclides. Half-life values obtained are 53·09 ± 0·09 hr for $^{149}$Pm and 28·40 ± 0·04 hr for $^{151}$Pm.

$\gamma$-Ray scintillation spectrometry showed only one prominent $\gamma$-ray in the decay of $^{149}$Pm at 286 keV. This $\gamma$-ray is present in about 2 per cent abundance. $^{151}$Pm exhibited prominent $\gamma$-rays at 71, 108, 170, 342 and 442 keV.

HALF-LIFE values for $^{149}$Pm as reported in the literature[1,2] vary from 47 to 55 hr. Only one measurement for the half-life of $^{151}$Pm is reported, 27·5 hr.[2] In addition, information on $\gamma$-ray abundances in $^{149}$Pm is meagre.

In order to measure the half-lives of these radionuclides, simultaneous irradiations of enriched $^{148}$Nd and $^{150}$Nd in individual quartz capsules were carried out. The $^{149}$Pm and the $^{151}$Pm resulting from these bombardments were purified and the half-lives measured by direct decay measurements on several different types of counting instruments. Corrections were applied to the data, when necessary, for the activity contributions from small amounts of $^{147}$Pm and for $^{149}$Pm and $^{151}$Pm when they were contaminants of each other.

## 1. EXPERIMENTAL DETAILS

Ten milligrams each of enriched $^{148}$Nd (89%) and $^{150}$Nd (95%) were irradiated in a high flux region of the Materials Testing Reactor to form $^{149}$Nd and $^{151}$Nd by the $(n, \gamma)$ reaction. Subsequent $\beta$-decay of these Nd isotopes gave $^{149}$Pm and $^{151}$Pm.

$$^{148}\text{Nd} \xrightarrow{n,\gamma} {}^{149}\text{Nd} \xrightarrow{T_{1/2}=1{\cdot}8\ \text{hr}} {}^{149}\text{Pm} \longrightarrow {}^{149}\text{Sm (stable)}$$

$$^{150}\text{Nd} \xrightarrow{n,\gamma} {}^{151}\text{Nd} \xrightarrow{T_{1/2}=15\ \text{min}} {}^{151}\text{Pm} \longrightarrow {}^{151}\text{Sm} \xrightarrow{T_{1/2}=80\ \text{years}} {}^{151}\text{Eu (stable)}$$

The Pm isotopes were separated from the Nd and activated rare-earth impurities by ion exchange chromatography.[3] A centre cut of the Pm fraction from each of the samples was diluted to an arbitrary volume and measured aliquots were taken from each and prepared for counting in a manner dependent upon the instrument to be used.

For measurements made in a high-pressure $\gamma$-ray ionization chamber[4,5] the aliquots were evaporated to dryness in 50 ml lusteroid tubes. A similar procedure, with 20 ml lusteroid tubes, was used for samples followed on a well-type $\gamma$-ray scintillation counter. For counting in a $4\pi$ geometry $\beta$-proportional counter aliquots were evaporated on VYNS films which had been gold-plated on both sides. Samples were prepared for counting on flow-type, side-window $\beta$-proportional counters by adding inactive Nd carrier in known amounts and then precipitating Nd oxalate by the addition of

[1] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Table of Isotopes*, *Rev. Mod. Phys.* **30**, 585 (1958).
[2] W. C. RUTLEDGE, J. M. CORK and S. B. BURSON, *Phys. Rev.* **86**, 775 (1952).
[3] L. R. BUNNEY, E. C. FREILING, L. D. MCISAAC and E. M. SCADDEN, *Nucleonics* **15**, No. 2, 81 (1957).
[4] J. W. JONES and R. J. OVERMAN, AECD-2367 (1948).
[5] C. BORKOWSKI, *Analyt. Chem.* **21**, No. 3, 350 (1949).



Vol. 12 1959/6

ammonium oxalate[5] so that the corrections for contaminants obtained from the larger aliquot could be applied to the smaller aliquots by adjusting for chemical yield and aliquot size. The Nd oxalate was filtered onto a weighed Whatman No. 42 filter paper, 2·3 cm in diameter. The precipitates were washed, dried, weighed and mounted on brass planchets for the decay measurements. The initial counting data for the $^{151}$Pm samples was obtained as soon as possible after the irradiation in order to minimize any $^{149}$Pm contamination.

The initial decay points were obtained approximately 60 hr after irradiation in the case of $^{151}$Pm. The $^{149}$Pm samples were allowed to decay for a period of 12·5 days before utilizing the counting data

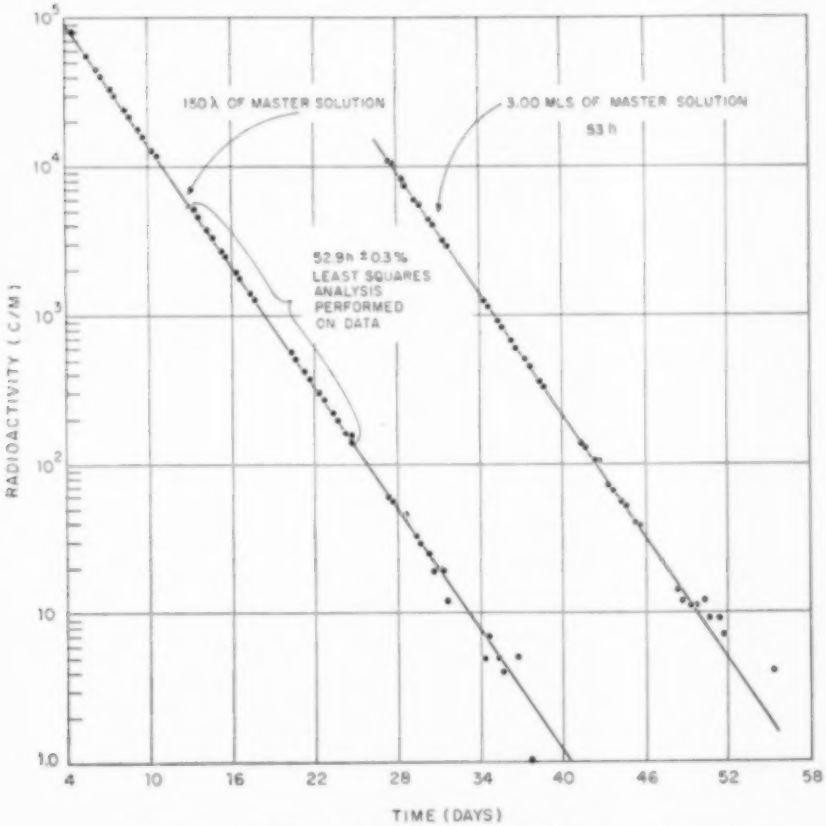



FIG. 1.—Decay of $^{149}$Pm followed on a flow-type, side-window $\beta$-proportional counter through 42·5 mg/cm$^2$ of Al.

for half-life calculations in order to minimize any $^{151}$Pm contamination. Where long-lived, low-level contaminating activities, such as $^{147}$Pm, were present, the appropriate corrections to the decay data were made from measured aliquots which were very much larger than the original ones. This permitted these corrections to be made with a greater accuracy than would have been possible using the original aliquots. Where appropriate, analytical methods[6] were used to obtain the correction. After the corrections to the counting data had been made, the data from the $^{149}$Pm samples which were counted in the flow-type, side-window $\beta$-proportional counter were submitted to a weighted least squares analysis, i.e. each point was weighted according to the total counts taken at that point. All other data from both $^{149}$Pm and $^{151}$Pm were submitted to the unweighted least squares analysis,

[6] E. C. FREILING and L. R. BUNNEY, *Nucleonics* **14**, No. 9, 112 (1956).

i.e. each point was given equal weight in the calculations regardless of how many counts had been taken at that point. The unweighted least squares analyses were performed on those systems which had three components since a generally accepted method for performing a weighted analysis on such systems has not been developed.

Figs. 1, 2 and 3 are representative examples of two of the different methods of obtaining decay data for the two isotopes. Fig. 1 presents the decay data for two of the aliquots of $^{149}$Pm which were counted in the flow-type, side-window $\beta$-proportional

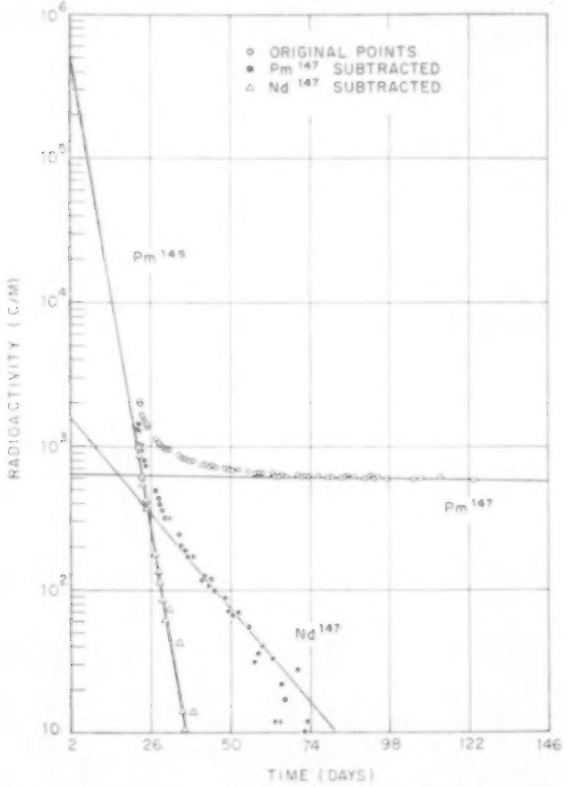



Fig. 2.—Decay of 5·00 ml of $^{151}$Pm master solution followed on a well-type $\gamma$-scintillation counter.

counter. These particular aliquots differ in volume by a factor of twenty. Their decay was followed for a total of sixty days: through 14·9 half-lives for the smaller aliquot taking forty-nine points and through 16·8 half-lives for the larger aliquot, which was withdrawn twenty-four days later, taking sixty points. As can be seen from the graph, the $^{149}$Pm activity decayed through a factor of $10^7$ or twenty-five half-lives without any detectable contamination appearing. Any $^{147}$Pm contamination was minimized by counting through 42·5 mg/cm$^2$ of Al.

Figs. 2 and 3 present the decay data of two of the $^{151}$Pm aliquots which were counted in the well-type $\gamma$-scintillation counter. Fig. 3 is the decay plot of one of the original aliquots and Fig. 2 is the decay plot of the larger aliquot which was withdrawn twenty-two days later. From these two graphs, it can be determined that in the

Vol. 12 1959/6

region where the half-life of $^{151}$Pm was measured (about 2–11 days after irradiation), the contribution of $^{147}$Pm and $^{147}$Nd together to the total activity rose from 0·002 to 0·3 per cent and the contribution of $^{149}$Pm rose from 0·52 to 5·2 per cent. Only the $^{149}$Pm activity was subtracted from the original decay points to obtain the data for the half-life determination of $^{151}$Pm since the $^{147}$Nd and $^{147}$Pm contributions were

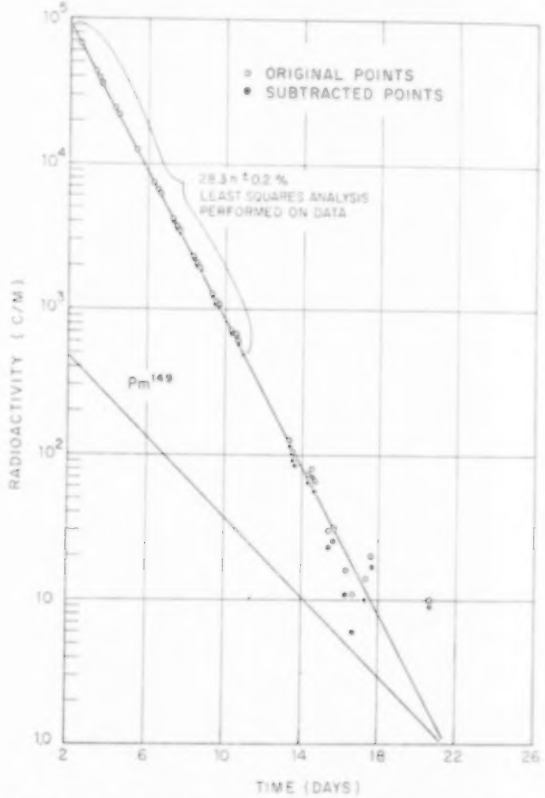



FIG. 3.—Decay of 0·005 ml of $^{151}$Pm master solution followed on a well-type γ-scintillation counter.

insignificant in that region. The amount of $^{149}$Pm activity subtracted from the total activity in each of the smaller aliquots was calculated on a direct ratio basis. This is shown in Fig. 3 which shows the original decay points, the contribution of $^{149}$Pm to the total activity and the subtracted points.

## 2. RESULTS

The results obtained for $^{149}$Pm and $^{151}$Pm are presented in Tables 1 and 2, respectively. The uncertainty quoted is the standard deviation of each complete set of measurements. In obtaining the average, each individual determination was weighted by the reciprocal of the standard deviation of the individual points from the line obtained by least squares analysis.

γ-Ray pulse height distributions were obtained on a single channel scintillation

Table 1.—Results of $^{149}$Pm half-life determinations

| Determination no. | Std. dev. of decay points | Half-life (hr) | Counting instrument |
|---|---|---|---|
| 1 | 0·0034 | 52·77 | Side-window $\beta$-proportional counter |
| 2 | 0·0028 | 53·00 | |
| 3 | 0·0034 | 52·94 | |
| 4 | 0·0034 | 52·70 | |
| 5 | 0·0018 | 53·40 | $4\pi$ beta proportional counter |
| 6 | 0·0010 | 53·12 | |
| Weighted av. | | 53·09 ± 0·09 | |

Table 2.—Results of $^{151}$Pm half-life determinations

| Determination no. | Std. dev. of decay points | Half-life (hr) | Counting instrument |
|---|---|---|---|
| 1 | 0·002 | 28·35 | Side-window $\beta$-proportional counter |
| 2 | 0·002 | 28·49 | |
| 3 | 0·003 | 28·44 | |
| 4 | 0·002 | 28·56 | |
| 5 | 0·001 | 28·36 | Well-type $\gamma$-scintillation counter |
| 6 | 0·002 | 28·25 | |
| 7 | 0·002 | 28·33 | |
| 8 | 0·002 | 28·30 | |
| 9 | 0·003 | 28·67 | High-pressure $\gamma$-ionization chamber |
| 10 | 0·002 | 28·55 | |
| Weighted av. | | 28·40 ± 0·04 | |

Table 3.—Prominent $\gamma$-rays observed in the decay of $^{149}$Pm and $^{151}$Pm

| | $\gamma$-Ray energies (MeV) |
|---|---|
| $^{149}$Pm | 0·286 |
| $^{151}$Pm | 0·071, 0·108, 0·170, 0·342, 0·442 |

spectrometer, equipped with a 2 × 2 in. NaI(Tl) crystal, to observe the prominent $\gamma$-rays present in the decay of the two nuclides. They are listed in Table 3.

The $\gamma$-ray spectrum of $^{149}$Pm showed only one prominent peak. This occurred at 286 keV. An estimate of its $\gamma$-emission rate in a known aliquot was obtained from

Vol. 12 1959/60

measurements on a NaI(Tl) scintillation spectrometer previously calibrated for $\gamma$-ray counting efficiency vs. $\gamma$-ray energy. The $\beta$-ray disintegration rate was measured on another aliquot on a $4\pi$ geometry proportional counter. From these measurements the abundance of the 286 keV $\gamma$-ray was calculated to be $1{\cdot}5 \pm 0{\cdot}5$ per cent.

It might be noted that previous studies[2,7] of $^{151}$Pm have not included chemical separations of Pm. The work reported here thus confirms the identification of the 28·4 hr species as an isotope of promethium.

[7] H. S. Hans, B. Saraf and C. E. Mandeville, *Phys. Rev.* **97**, 1267 (1955); **98**, 1173A (1955).

ol.
12
9/60

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 234 to 235. Pergamon Press Ltd. Printed in Northern Ireland

# THE SPECIFIC ACTIVITY AND HALF-LIFE OF $^{237}Np$

F. P. BRAUER, R. W. STROMATT, J. D. LUDWICK, F. P. ROBERTS and W. L. LYON
Hanford Atomic Products Operation*
General Electric Company, Richland, Washington

(*Received* 22 *May* 1959)

**Abstract**—The specific activity of $^{237}Np$, as determined by absolute α-counting known amounts of $^{237}Np$, was found to be 1562 ± 7 disintegrations per min per μg which corresponds to a half-life of 2·14 ± 0·01 × $10^6$ years. The aliquots of $^{237}Np$ for counting were taken from a standard solution prepared from neptunium metal and checked by coulometric titration.

THE reported specific activity value of 1520 disintegrations per min per μg for $^{237}Np$ based on ultramicro weighings of $NpO_2$ and 2π α-counting has been estimated to be probably accurate to within five per cent.[1] In the experiments described below the specific activity of $^{237}Np$ was determined by absolute α-counting known amounts of $^{237}Np$ using both low geometry proportional counting and 4π liquid scintillation counting. The aliquots of $^{237}Np$ were taken from a standard solution prepared from neptunium metal and checked by controlled potential coulometric titration. The observed α-disintegration rate was corrected for the contribution of the plutonium impurity as determined by α-energy analysis. The neptunium used was analysed isotopically to insure that isotopes other than $^{237}Np$ were present at a sufficiently low concentration to be neglected.

Vol.
12
1959/6

## EXPERIMENTAL

Neptunium(IV) oxalate was precipitated from a neptunium nitrate solution purified by anion exchange to remove traces of other actinide element impurities. The oxalate was converted to the fluoride with anhydrous HF. Neptunium metal was prepared by reduction of the fluoride with high purity calcium, using iodine as a booster, in a magnesia-lined bomb. After remelting and casting under high vacuum for further purification, the neptunium metal was machined in order to obtain an oxide-free metal specimen which was immediately weighed, dissolved and diluted to a known volume. The impurities in the metal as determined by spectrochemical analysis and α-energy analysis were found to be 0·03 weight per cent. The concentration of the standard $^{237}Np$ solution was checked within 0·05 per cent by titration using a controlled potential coulometer.[2] An isotopic analysis by mass spectrometry established that no significant amounts of neptunium isotopes other than $^{237}Np$ were present.

Four $^{237}Np$ sources mounted on polished platinum disks were α-counted in a low geometry α-counter similar to that described by JAFFEY.[3] The calibration of the instrument had been checked in recent years by exchanging mounted α-samples with both UCRL and ANL.[4, 5] Two scintillation solutions containing aliquots of the $^{237}Np$ standard were counted by 4π liquid scintillation α-counting

* Operated for the Atomic Energy Commission by the General Electric Company under Contract # W-31-109-Eng-52.

(1) L. B. MAGNUSSON and T. J. LA CHAPELLE, *The Transuranium Elements* (Edited by G. T. SEABORG and J. J. KATZ) NNES, Plutonium Project Record, Div. IV, Vol. 14B, p. 39. McGraw-Hill, New York (1949).
(2) R. W. STROMATT, *The Determination of Neptunium by Controlled Potential Coulometry*, HW-59449 (1959).
(3) A. H. JAFFEY, *The Actinide Elements* (Edited by G. T. SEABORG and J. J. KATZ) NNES, Plutonium Project Record, Div. IV, Vol. 14A, p. 596. McGraw-Hill, New York (1954).
(4) H. P. ROBINSON. Private communication (1956).
(5) R. F. BUCHANAN. Private communication (1957).

techniques. Complete resolution between the daughter $^{233}Pa$ $\beta$-particles and $^{237}Np$ $\alpha$-particles was obtained and no quenching resulted with sample addition to the scintillator. Calibrated glassware was used for all volume measurements and all dilutions of the primary standard were checked by coulometric titration so that the weights of $^{237}Np$ on the $\alpha$-disks and in the scintillator solutions were accurately known. The counting data are summarized in Table 1. The average observed decay rate was $1583 \pm 6$ disintegrations per min per $\mu$g of neptunium. The uncertainties listed in the table for the observed disintegration rates are based on the counting statistics at the 95 per cent confidence level. The uncertainty given for the average value of the specific activity is the estimated precision at the 95 per cent confidence level for the average of the six results.

A gridded ion chamber was used for $\alpha$-energy analysis of several aliquots of the standard $^{237}Np$ solutions. The $\alpha$-spectrum showed that the $\alpha$-activity of the solution was 98·7 per cent $^{237}Np$ within an estimated error of $\pm 0{\cdot}2$ per cent and that the remaining $\alpha$-activity was due to plutonium impurity.

TABLE 1.—OBSERVED $\alpha$-ACTIVITY

| Source | Method of counting | Weight of $^{237}Np$ ($\mu$g) | Observed disintegration $min^{-1}$ | Disintegration $min^{-1}\ \mu g^{-1}$ |
|---|---|---|---|---|
| A | low geometry | 147·35 | 234,360 ± 420 | 1591 |
| B | low geometry | 294·91 | 467,730 ± 520 | 1586 |
| C | low geometry | 147·35 | 231,890 ± 320 | 1574 |
| D | low geometry | 73·64 | 116,840 ± 360 | 1587 |
| E | $4\pi$ L.S.S. | 9·349 | 14,803 ± 34 | 1583 |
| F | $4\pi$ L.S.S. | 9·349 | 14,729 ± 54 | 1575 |
| | | | Average | 1583 ± 6 |

## RESULTS

The observed specific activity of $1583 \pm 6$ disintegrations per min per $\mu$g of neptunium multiplied by the observed alpha per cent $^{237}Np$ of $98{\cdot}7 \pm 0{\cdot}2$ gives a value of $1562 \pm 7$ disintegrations per min per $\mu$g for the $^{237}Np$ specific activity. Using the radioactive decay law a value for the half-life of $^{237}Np$ of $2{\cdot}14 \pm 0{\cdot}01 \times 10^6$ years is obtained in agreement with the value of $2{\cdot}2 \pm 0{\cdot}1 \times 10^6$ years reported by MAGNUSSON and LA CHAPELLE.[1]

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 236 to 240. Pergamon Press Ltd. Printed in Northern Ireland

# TWO NEW NEUTRON-DEFICIENT TERBIUM ACTIVITIES*

K. S. Toth† and J. O. Rasmussen
Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California

(*Received* 3 *November* 1958)

**Abstract**—A series of $^{12}C$ bombardments on $^{141}Pr$ has resulted in the discovery of two new activities. The first, with a 70 min half-life, is believed to be $^{148}Tb$. The isotope has two $\gamma$-rays, 780 and 1120 keV, following its decay. The 780 keV $\gamma$-ray is postulated to be the transition from the first excited level to the ground state in the even-even nucleus, $^{148}Gd$. The second activity has a half-life of 24 min and has a 305 keV $\gamma$-ray following its decay. It is probably $^{147}Tb$, though this has not been clearly established.

Praseodymium-141 has been bombarded with $^{12}C$ ions at the heavy-ion linear accelerator, and two activities have been observed that had not been described hitherto. These activities are probably $^{148}Tb$ and $^{147}Tb$.

*Terbium*-148

A 70 min half-life was first identified in a 110 MeV $^{14}N$ bombardment on $^{141}Pr$. At that time it was uncertain whether the activity belonged to a dysprosium or a terbium isotope. The possibility of its being a dysprosium isotope was ruled out when the half-life was observed in a $^{12}C$ bombardment on the same material. In this particular experiment the rare earths were separated from one another by an ion-exchange method described elsewhere.[1] The 70 min half-life was seen in the same fraction as the 4 hr $^{149}Tb$, so that the new activity was certainly a terbium isotope.

The mass-assignment of the new activity was accomplished in the following manner: By repeating the above-described experiment, including the ion-exchange chemical separation, using $^{12}C$ ions of a different energy, we could determine that the mass number of the new activity was less than that of $^{149}Tb$. $\gamma$-spectra were obtained in both bombardments, and it was observed that the $\gamma$-rays of $^{149}Tb$ were present in lesser amounts in the experiment carried out at the higher energy. The reverse was true of the $\gamma$-rays assigned to the new activity. The energies of the $^{12}C$ ions in the two experiments were approximately 65 and 75 MeV. The decay of $^{147}Gd$ has been well studied, so that its $\gamma$-ray energies are known.[2] None of the $^{147}Gd$ $\gamma$-rays appeared in the $\gamma$-spectra taken with the above sample. The $\gamma$-rays of $^{149}Gd$ growing in from $^{149}Tb$ were observed. The inability to see any $^{147}Gd$ growing in from a pure terbium fraction certainly indicates that the new activity could not be $^{147}Tb$. $^{148}Gd$ has a half-life of about 130 years. No $\gamma$-rays have been identified in connexion with its decay. The isotope is an $\alpha$-emitter, and there is also fair evidence that it is $\beta$-stable.[3]

* This work was performed under the auspices of the U.S. Atomic Energy Commission.
† Present address: Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[1] S. G. Thompson, B. G. Harvey, G. R. Choppin and G. T. Seaborg, *J. Amer. Chem. Soc.* **76**, 6229 (1954).
[2] V. S. Shirley, W. G. Smith and J. O. Rasmussen, *Nucl. Phys.* **4**, 395 (1957).
[3] M. A. Rollier and J. O. Rasmussen (UCRL). Unpublished data.



Vol.
12
1959/6

Its half-life is too long for growth of its activity to be seen with samples containing originally the 70 min activity.

The next experiment performed was a bombardment of $^{141}$Pr with 100 MeV $^{12}$C ions. The results from this experiment are discussed more fully in connexion with $^{147}$Tb. Suffice it to say that the $\gamma$-spectrum in this case indicated that $^{147}$Gd, presumably growing in from $^{147}$Tb, was present in large quantity, while $^{149}$Tb was definitely absent and the $\gamma$-rays assigned to the 70 min activity were present, if at all, to a very limited extent. Essentially the same kind of evidence was obtained from $^{14}$N bombardments on $^{141}$Pr. In these experiments no chemical separations were made. Terbium-149 was seen to be present in an 80 MeV bombardment but the $\gamma$-rays of the 70 min activity were not. In a 110 MeV $^{14}$N bombardment the $\gamma$-rays of the new activity were very much in evidence, being in greater abundance than the $\gamma$-rays of $^{149}$Tb.

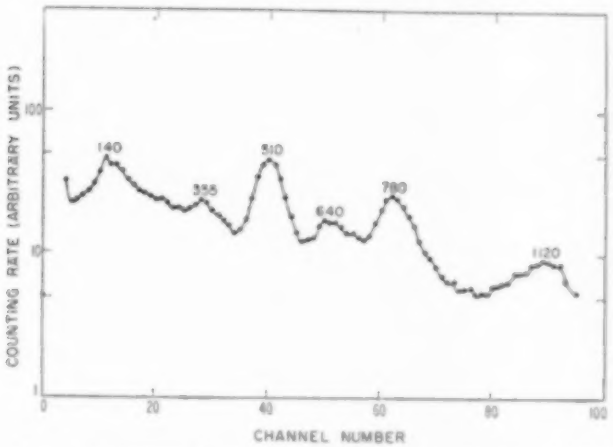



FIG. 1.—$\gamma$-Spectrum obtained in the 75 MeV $^{12}$C bombardment on $^{141}$Pr.

Spectra of the same sample taken at later times did not show any $^{147}$Gd present, while $^{149}$Gd was seen. A 225 keV $\gamma$-ray very prominent in $^{147}$Gd decay was definitely absent from this experiment. The evidence from the two $^{14}$N bombardments together with that from the $^{12}$C experiments indicates that the 70 min activity has a lesser mass number than that of $^{149}$Tb, but presumably greater than 147. In this manner the 70 min activity was determined to be $^{148}$Tb.

The $\gamma$-spectrum obtained in the 75 MeV $^{12}$C bombardment is shown in Fig. 1. The two $\gamma$-rays assigned to the decay of $^{148}$Tb have energies of 780 and 1120 keV. The half-lives of the two peaks were determined and found to be about 70 min. The two $\gamma$-rays have thus been assigned to $^{148}$Tb decay, not only on the basis of the variation of their intensities with bombarding energies, but also because of their half-lives. Table 1 lists the first-excited-level energies of even-even nuclei whose neutron numbers vary from 90 to 82.

The energies quoted for all these nuclei are well established and have been taken from the new Table of Isotopes.[4] The variation of first-excited-level energies of even-even nuclei with neutron number is readily noted. As the neutron number is

[4] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).

decreased going from the region where rotational levels in nuclei are observed toward the 82-neutron closed shell, the energies increase. They begin to decrease again on the other side of the 82-neutron shell, though this is not shown in Table 1. $^{148}$Gd, the nucleus populated in the decay of $^{148}$Tb, has 84 neutrons, the same number as $^{144}$Nd. For that reason one would expect that their first-excited-level energies would be somewhat similar in magnitude. The first excited level in $^{144}$Nd has an energy of 694 keV. When we note another general trend in Table 1—that is, that the energies

Table 1.—Variation of energy of first-excited-level with neutron number

| Neutron number | Nucleus | Energy of first-excited-level in keV |
|---|---|---|
| 90 | $^{154}$Gd | 123 |
| | $^{152}$Sm | 122 |
| 88 | $^{152}$Gd | 344 |
| | $^{150}$Sm | 337 |
| 86 | $^{148}$Sm | 562 |
| | $^{146}$Nd | 460 |
| 84 | $^{144}$Nd | 694 |
| 83 | $^{143}$Nd | 1570 |
| | $^{140}$Ce | 1596 |
| | $^{138}$Ba | 1430 |
| | $^{136}$Xe | 1320 |

seem to increase with atomic number for a given neutron number—it certainly does not seem unreasonable to propose that the 780 keV $\gamma$-ray in $^{148}$Tb decay represents the transition from the first excited level to the ground state in $^{148}$Gd. The ratio of intensities of the two $\gamma$-rays, 780 and 1120 keV, assigned to $^{148}$Tb is 8 : 5, after the $\gamma$-ray intensities have been corrected for the efficiency of the 3 $\times$ 3 in. NaI(Tl) crystal used to obtain the spectra. We should like to suggest that the two $\gamma$-rays may be in cascade, with the 1120 keV $\gamma$-ray being the transition from a level at about 1900 keV to the 780 keV first excited state. A somewhat analogous case exists in $^{144}$Nd, in which a transition of 1490 keV proceeds from a level at 2180 keV down to the first excited level at 694 keV. Coincidence work is needed to test this possibility.

The rest of the $\gamma$-rays in the spectrum were found to decay with a 4 hr half-life. A spectrum taken approximately 10 hr after the one displayed in Fig. 1 was obtained showed no peaks at 780 or 1120 keV. Only the $\gamma$-rays of $^{149}$Tb were visible.

The decay curves of the 510 keV and $K$ X-ray peaks were resolved and found to have 70 min components. Thus the 70 min activity must decay both by positron emission and by electron capture.

*Terbium*-147

A new activity with a half-life of 24 min was observed in the 100 MeV $^{12}$C bombardment on $^{141}$Pr. As mentioned previously, $^{147}$Gd was known to be certainly present

Vol. 12 1959/60

in the sample produced from this bombardment by virtue of the identification of its $\gamma$-rays, while $^{149}$Tb and $^{148}$Tb were known to be absent. Fig. 2 shows the $\gamma$-spectrum taken of the sample approximately 10 min after the termination of the bombardment. The $\gamma$-rays of $^{149}$Tb and $^{148}$Tb are not observed in the spectrum. There is a peak at 225 keV which represents the most prominent $\gamma$-ray in $^{147}$Gd decay. There are also

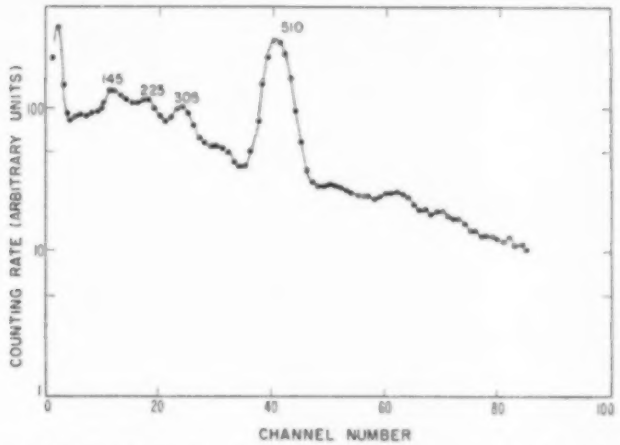



FIG. 2.—$\gamma$-Spectrum obtained in the 100 MeV $^{12}$C bombardment on $^{141}$Pr. The spectrum was taken approximately 10 min after the termination of the bombardment.

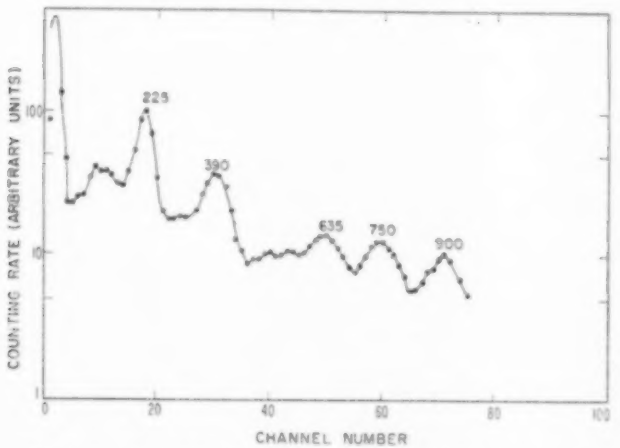



FIG. 3.—$\gamma$-Spectrum taken a day after the termination of the 100 MeV $^{12}$C bombardment on $^{141}$Pr. The prominent $\gamma$-rays in the decay of $^{147}$Gd are readily observed.

two other peaks present, one at 145 and the other at 305 keV. The half-life of the 305 keV $\gamma$-ray was found to be 24 min. There was a component of about the same half-life in the decay curve of the 145 keV peak. Spectra taken at later times showed the 225 keV $\gamma$-ray increasing in intensity relative to the other two peaks, and at still later times the remainder of the $^{147}$Gd $\gamma$-rays became evident. The same 24 min half-life appeared as the shortest component of both the Geiger–Müller counter and the 510 keV annihilation peak decay curves.

Thus it was established that a new activity with at least one $\gamma$-ray (305 keV) had been found. Also the mass number of the isotope had to be less than 148 because the 305 keV $\gamma$-ray belonging to its decay was not seen in the 65 and 75 MeV $^{12}C$ bombardments when $^{148}Tb$ was known to be present. We would like to propose that the new isotope is $^{147}Tb$ for the following two reasons:

(1) The decay curve of the 225 keV $\gamma$-ray was obtained and it was found to have an initial interval of growth which was then followed by the characteristic half-life of $^{147}Gd$. The half-life of the growth period of the 225 keV $\gamma$-ray was found to be between 20 and 30 min, indicating that perhaps the $\gamma$-ray had grown in from the 24 min activity.

(2) In Fig. 3, which shows the spectrum taken a day after bombardment time, only the prominent $\gamma$-rays of $^{147}Gd$ decay are seen. Their energies are 225, 390, 635, 750 and 900 keV. Smaller peaks are seen at about 110, 120 and 500 keV, which represent undoubtedly some of the less intense $\gamma$-rays of approximately the same energies reported for $^{147}Gd$.[2] The point that we wish to emphasize is that no intense $\gamma$-rays, other than those of $^{147}Gd$, are visible, indicating that the 24 min activity probably does decay to $^{147}Gd$.

*Acknowledgements*—We should like to acknowledge the help and co-operation of the crew of the Berkeley heavy-ion linear accelerator. The assistance of the Health Chemistry Department of the Radiation Laboratory in monitoring and target transportation is also appreciated.

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 241 to 251. Pergamon Press Ltd. Printed in Northern Ireland

# THE USE OF ELECTRICAL CONDUCTIVITY DATA WITH JOB'S METHOD

J. F. TATE and M. M. JONES
Dept. of Chemistry, Vanderbilt University, Nashville, Tennessee

(*Received* 20 *May* 1959)

**Abstract**—The popularity of Job's method is to some extent based upon the large number of physical properties which are thought to be suitable for use with it. Among these properties, the electrical conductivity has enjoyed some popularity but has led to results which are often at variance with the results of studies using other properties or other methods. In order to find the source of this discord, a thorough theoretical and experimental analysis of this particular procedure has been performed.

THE use of electrical conductivity data with Job's method is usually justified by the claim that the specific conductance of a mixture of electrolytes is a linear function of the concentration of the various species present in solution. When this claim is investigated in more detail, it is found to be true only over certain ranges of concentration for most electrolytes. The variation of equivalent conductance ($\Lambda$) with concentration ($C$) or with ionic strength ($\mu$) has been represented by expressions such as[1,2]

$$\Lambda = \Lambda_0 - a\sqrt{C} \quad \text{or} \quad \Lambda = \Lambda_0 - a\sqrt{\mu} \tag{1}$$

$$\Lambda = \Lambda_0 - [\beta\Lambda_0 - \delta]\sqrt{\mu} \tag{2}$$

$$\Lambda = \Lambda_0 - BC^n \tag{3}$$

This last equation has been used successfully to represent the concentration dependence of dozens of electrolytes. In all cases, $n$ is less than unity. Since $\Lambda = 1000\,K/C$, the specific conductance, $K$ will generally not show a simple linear dependence on the concentration over wide ranges of this variable. The effect of this on studies with Job's method can be seen from the following considerations.

We will assume that the solutions for the study are prepared in the usual manner: by mixing $(1 - x)V$ ml of M molar A and $xV$ ml of M molar B to give solutions of total molarity M and total volume $V$. Volume changes in such a process can be accommodated by using a slightly different method of preparing the solutions[3] and do not constitute a serious limitation. The reaction in solution may be conveniently taken to be a simple one such as:

$$\mathrm{A} + n\mathrm{B} \rightleftharpoons \mathrm{AB}_n. \tag{4}$$

The usual method of continuous variations treatment[4,5] then shows that the concentration of the complex $AB_n$, will be a maximum in that solution for which $n = x/(1 - x)$. For a physical property which is a strictly linear function of the concentrations of A, B, and $AB_n$, it is found that the deviation from additivity of this property reaches an extremum at this same value of $x$. The deviation from additivity is simply the measured value of the property for the solution minus the predicted value based

[1] G. CHARLOT and R. GAGUIN, *Les Methodes D'Analyse Des Reactions En Solution*, p. 135ff. Masson et Cie, Paris (1951).
[2] A. I. VOGEL and A. FERGUSON, *Phil. Mag.* **50**, 971, 1163 (1925); **52**, 300, 941 (1927).
[3] M. M. JONES and K. K. INNES, *J. Phys. Chem.* **62**, 1005 (1958).
[4] P. JOB, *Ann. Chim.* [10] **9**, 113 (1928); [11], **6**, 97 (1936).
[5] W. C. VOSBURGH and G. R. COOPER, *J. Amer. Chem. Soc.* **63**, 437 (1941).

upon no reaction between A and B. This coincidence of extrema *must* be established for any property before it can be used with Job's method.

Job's method has been used with specific conductance data by many authors.[6-11] However, no complete evaluation of this procedure has yet been published. HAGENMULLER[11] alone realized that its use in a simple form was unjustified. In many instances the results obtained by conductance studies are in direct conflict with results obtained by other methods. The basic feature of these studies has been that the deviations of the specific conductances of the solutions from additivity are assumed to be significant in terms of chemical reactions.

When dealing with these solutions we may define $Y$ or the difference of the measured and predicted specific conductivity of the solutions as:

$$Y = K_1 + K_2 + K_3 - K_1' - K_2' \tag{5}$$

Here $K_1$, $K_2$, and $K_3$ are the specific conductances of A, B and $AB_n$ respectively in the mixtures and $K_1'$ and $K_2'$ are the specific conductances of A and B in their pure solutions at a concentration whose total is equal to their total concentration in the mixture. The difficulty lies in the choice of suitable concentration dependences for the $K$'s. The concentration dependence of $Y$ can readily be determined by the use of equations (1), (2) or (3) and the analysis follows similar lines for all three equations. Using equations (1) and (4) we can obtain an expression for $Y$ in terms of the concentrations and constants for each of the species as:

$$\begin{aligned} Y = 10^{-3}\{&C_1(\Lambda_{0_1} - a_1\sqrt{\mu}) + C_2(\Lambda_{0_2} - a_2\sqrt{\mu}) + C_3(\Lambda_{0_3} - a_3\sqrt{\mu}) \\ &- M(1-x)(\Lambda_{0_1} - a_1\sqrt{\mu}) - Mx(\Lambda_{0_2} - a_2\sqrt{\mu})\} \end{aligned} \tag{6}$$

In equation (6), $C_1$, $C_2$ and $C_3$ are the concentrations of A, B and $AB_n$ respectively. Because of the way in which the solutions were prepared, we can write:

$$A = C_1 = M(1-x) - C_3 \tag{7}$$

$$B = C_2 = Mx - nC_3 \tag{8}$$

Substitution of equations (7) and (8) into (6) allows us to express $Y$ in terms of $C_3$, $x$ and various constants as follows:

$$\begin{aligned} Y = 10^{-3}\{&[M(1-x) - C_3](\Lambda_{0_1} - a_1\sqrt{\mu}) + (Mx - nC_3)(\Lambda_{0_2} - a_2\sqrt{\mu}) \\ &+ C_3(\Lambda_{0_3} - a_3\sqrt{\mu}) - M(1-x)(\Lambda_{0_1} - a_1\sqrt{\mu}) - Mx(\Lambda_{0_2} - a_2\sqrt{\mu})\} \end{aligned} \tag{9}$$

The necessary and sufficient condition that $Y$ have an extrema when $C_3$ is a maximum is that $dY/dx = 0$ when $dC_3/dx = 0$. Differentiating (9) and setting $dC_3/dx = 0$ leads to

$$\frac{dY}{dx} = 10^{-3}\left\{C_3(a_1 + na_2 - a_3)\frac{d\sqrt{\mu}}{dx}\right\} \tag{10}$$

So, extrema in $Y$ will not generally coincide with extrema in $C_3$ unless $d\sqrt{(\mu)}/dx = 0$ also. When systems where this condition is also satisfied are examined it is seen that other complications are present (see Results and Discussion). The examination of systems where the concentration dependence follows equations (2) or (3) leads to analogous results.

[6] A. K. MUKHERJI and A. K. DEY, *J. Inorg. Nucl. Chem.* **6**, 314 (1958).
[7] A. K. MUKHERJI and A. K. DEY, *J. Indian Chem. Soc.* **35**, 237 (1958).
[8] B. C. PURKAYASTHA and R. N. SEN-SARMA, *J. Indian Chem. Soc.* **23**, 31 (1946).
[9] B. C. PURKAYASTHA, *J. Indian Chem. Soc.* **24**, 257 (1947); **25**, 81 (1948).
[10] Y. WORMSER, *Bull. Soc. Chim.* **15**, 395 (1948).
[11] P. HAGENMULLER, *Ann. Chim.* **6**, 5 (1951).

Vol. 12 1959/6

## EXPERIMENTAL

The electrical conductivities were measured using a Wheatstone bridge with a Kohlrausch slide-wire, a 1000 c/s a.c. oscillator and a set of earphones for a detector. The cells used were of the Jones and Bollinger types and were calibrated using standard potassium chloride solutions.[12] For the measurements, the cells were immersed in a water bath maintained at 25 ± 0·02°C and the precision of the measurements is estimated to 0·1 per cent. De-ionized water was used as a solvent. Since the solutions studied were all fairly concentrated this introduced a negligible error.

## RESULTS AND DISCUSSION

A number of systems were examined to compare the results obtained where complexes are known to be absent with results for systems in which complexes are known to be present. The systems studied were the $LiCl$–$CoCl_2$ system at total molar concentrations of 0·025 M, 0·1 M and 1·0 M; the $LiCl$–$BaCl_2$ system at 1·0 M; the $MgCl_2$–$CoCl_2$ system at 0·125 M; the $MnCl_2$–$Cu(NO_3)_2$ at 2 M, and the $Fe(NO_3)_3$–KCNS at 0·1 M.

SPECIFIC CONDUCTANCES OF PURE LiCl AND $CoCl_2$ SOLUTIONS

| Conc. (M/L) | LiCl $K \times 10^5$ | $CoCl_2$ $K \times 10^5$ |
|---|---|---|
| 0·02 | 208·3 | 417·5 |
| 0·04 | 402·5 | 787·9 |
| 0·06 | 591·7 | 1125 |
| 0·08 | 765·5 | 1500 |
| 0·1 | 953·6 | 1773 |
| 0·2 | 1783 | 3180 |
| 0·4 | 3425 | 5842 |
| 0·5 | 4150 | 6919 |
| 0·6 | 4794 | 7906 |
| 0·8 | 6134 | 9912 |
| 1·0 | 7328 | 11,170 |

SPECIFIC CONDUCTANCES OF MIXED LiCl AND $CoCl_2$ SOLUTIONS

| Mole ratio LiCl : $CoCl_2$ | Total M = 0·025 | | Total M = 0·1 | | Total M = 1·0 | |
|---|---|---|---|---|---|---|
| | $K \times 10^5$ | $Y \times 10^5$ | $K \times 10^5$ | $Y \times 10^5$ | $K \times 10^5$ | $Y \times 10^5$ |
| 1/9 | 487·7 | 6·8 | 1660 | 81·0 | 10,970 | 534 |
| 2/8 | 457·3 | 14·7 | 1602 | 107 | 10,490 | 1210 |
| 3/7 | 434·0 | 22·5 | 1538 | 55 | 10,200 | 1478 |
| 4/6 | 416·1 | 23·2 | 1464 | 64 | 10,000 | 1330 |
| 5/5 | 389·3 | 7·1 | 1341 | 45 | 9882 | 1188 |
| 6/4 | 362·6 | 44·4 | 1301 | 78 | 9026 | 2150 |
| 7/3 | 336·7 | 15·8 | 1195 | 73 | 8702 | 1568 |
| 8/2 | 309·7 | 11·4 | 1103 | 80 | 8190 | 1124 |
| 9/1 | 282·6 | 5·5 | 1038 | 59 | 7816 | 732 |

[12] *Apparatus for Electrolytic Conductivity Measurements in Laboratory and Plant.* Leeds and Northrup Co. Philadelphia (1944).

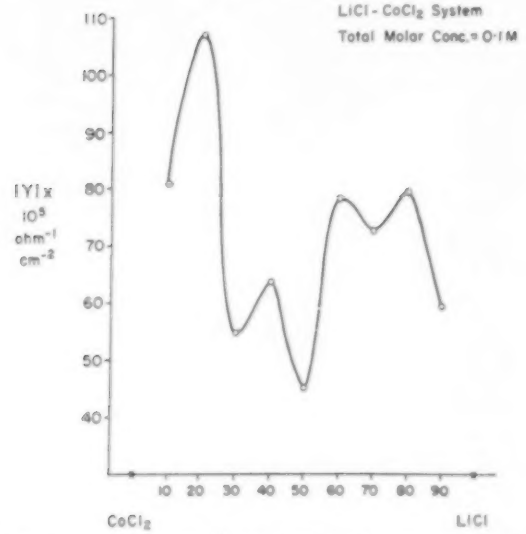



FIG. 1.—Deviation from additivity of specific conductance in mixtures of $LiCl–CoCl_2$.

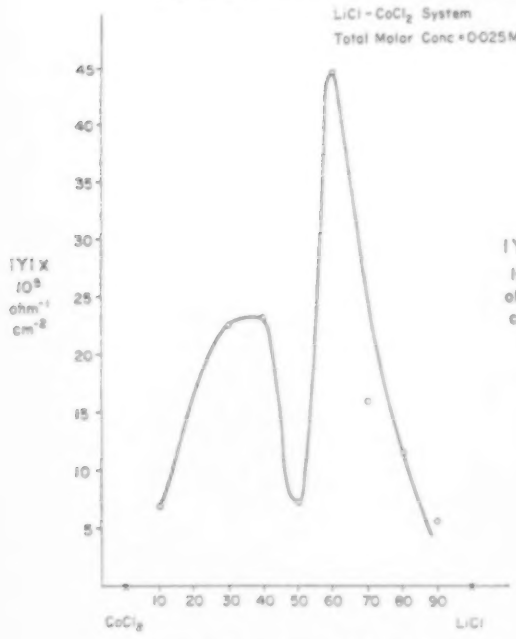



FIG. 2.—Deviation from additivity of specific conductance in mixtures of $LiCl–CoCl_2$.

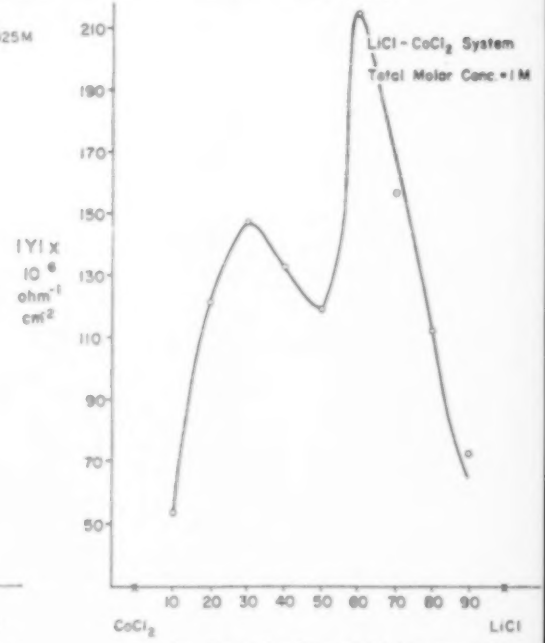



FIG. 3.—Deviation from additivity of specific conductance in mixtures of $LiCl–CoCl_2$.

In the $LiCl–CoCl_2$ system no appreciable formation of chloro-complex is expected at the concentrations studied.[13] Nevertheless, when $Y$ is plotted against $x$ for these systems (Figs. 1, 2 and 3) extrema are clearly indicated.

[13] J. BJERRUM, G. SCHWARZENBACH and L. G. SILLEN, *Stability Constants* Part II, p. 97. The Chemical Society, London (1958).

Vol. 12 1959/6

In the LiCl–$BaCl_2$ system again no complex is expected, yet the $Y$ vs. $x$ data show *two* extrema (Fig. 4). Neither of these corresponds to any complex established by any reliable procedure.

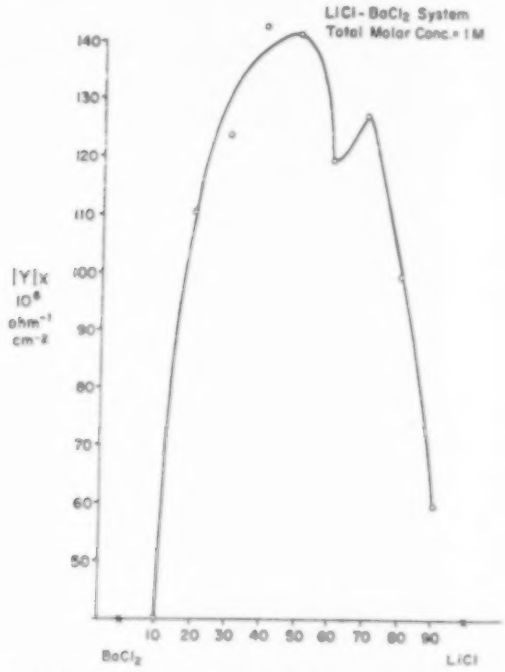



FIG. 4.—Deviation from additivity of specific conductance in mixtures of LiCl-$BaCl_2$.

SPECIFIC CONDUCTANCES OF $BaCl_2$ SOLUTIONS

| Conc. M/L | 0·1 | 0·2 | 0·4 | 0·5 | 0·6 | 0·8 | 1·0 |
|---|---|---|---|---|---|---|---|
| $K \times 10^5$ | 1944 | 3553 | 6382 | 8012 | 9344 | 11,770 | 13,830 |

SPECIFIC CONDUCTANCES OF MIXED LiCl AND $BaCl_2$ SOLUTIONS

| Mole ratio LiCl : $BaCl_2$ | Total M = 1·0, | |
|---|---|---|
| | $K \times 10^5$ | $Y \times 10^5$ |
| 1/9 | 12,960 | 392 |
| 2/8 | 12,450 | 1104 |
| 3/7 | 12,030 | 1240 |
| 4/6 | 11,340 | 1433 |
| 5/5 | 10,740 | 1418 |
| 6/4 | 9981 | 1195 |
| 7/3 | 9428 | 1272 |
| 8/2 | 8690 | 997 |
| 9/1 | 8030 | 595 |

In the $CoCl_2$–$MgCl_2$ system, an extremum is again found in a system containing no complex (Fig. 5).

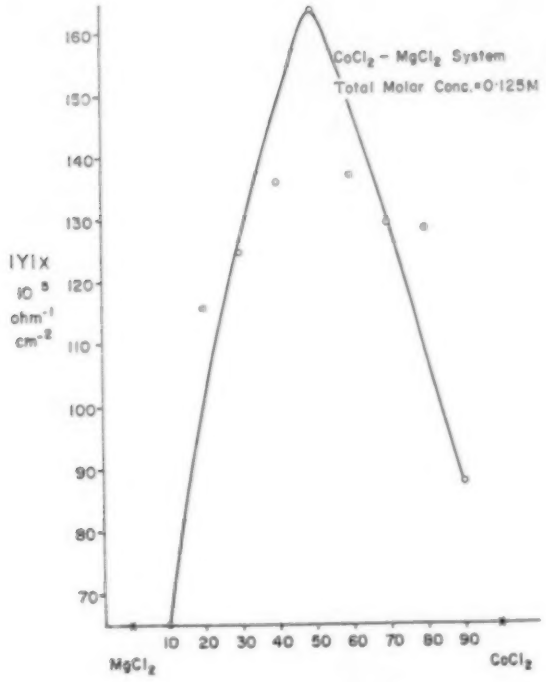



FIG. 5.—Deviation from additivity of specific conductance in mixtures of $CoCl_2$–$MgCl_2$.

SPECIFIC CONDUCTANCES OF $MgCl_2$ AND $CoCl_2$ SOLUTIONS

| Conc. (M/L) | 0·0125 | 0·025 | 0·05 | 0·0625 | 0·0875 | 0·100 | 0·125 |
|---|---|---|---|---|---|---|---|
| $MgCl_2$; $K \times 10^5$ | 272 | 512 | 964 | 1182 | 1600 | 1801 | 2164 |
| $CoCl_2$; $K \times 10^5$ | 271 | 514 | 965 | 1182 | 1604 | 1819 | 2194 |

SPECIFIC CONDUCTANCES OF $MgCl_2$–$CoCl_2$ MIXTURES (M = 0·125)

| Mole ratio $MgCl_2$ : $CoCl_2$ | 1/9 | 2/8 | 3/7 | 4/6 | 5/5 | 6/4 | 7/3 | 8/2 | 9/1 |
|---|---|---|---|---|---|---|---|---|---|
| $K \times 10^5$ | 2188 | 2194 | 2199 | 2197 | 2196 | 2197 | 2197 | 2197 | 2197 |
| $Y \times 10^5$ | 88 | 128 | 129 | 137 | 164 | 136 | 125 | 116 | 65 |

In the $MnCl_2$–$Cu(NO_3)_2$ system, a symmetrical $Y$ vs. $x$ curve is obtained with a maximum at $x = 0{\cdot}5$ (Fig. 6). This would indicate that the complex in solution is $CuCl_2$. From other work,[13] the ions $CuCl_3^-$ and $CuCl_4^{2-}$ are known to be important species in solutions of this concentration. This system was selected for study because of the nearly identical specific conductances of the *parent* solutions. In this case,

Vol. 12 1959/6

however, the variation of the specific conductance with concentration was very marked.

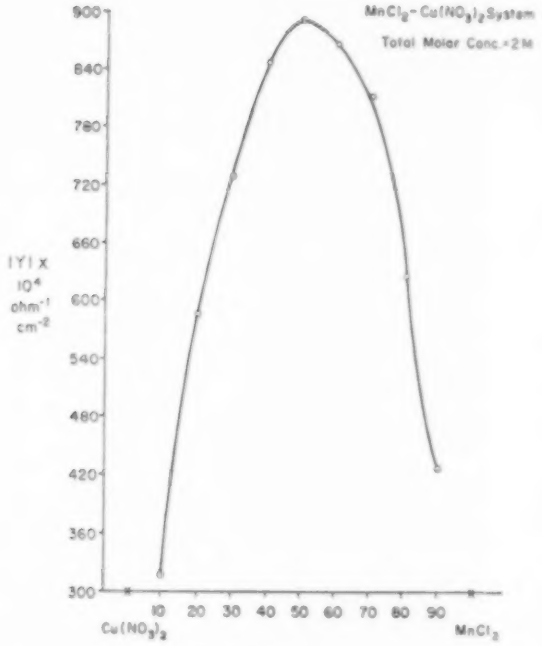



FIG. 6.—Deviation from additivity of specific conductance in mixtures of $MnCl_2$–$Cu(NO_3)_2$.

SPECIFIC CONDUCTANCES OF $MnCl_2$ AND $Cu(NO_3)_2$ SOLUTIONS

| Conc. (M/l.) | 0·2 | 0·4 | 0·8 | 1·0 | 1·2 | 1·4 | 1·8 |
|---|---|---|---|---|---|---|---|
| $MnCl_2$; $K \times 10^4$ | 303·4 | 587·3 | 935·0 | 1066 | 1165 | 1247 | 1347 |
| $Cu(NO_3)_2$; $K \times 10^4$ | 333·8 | 570·9 | 934·2 | 1055 | 1150 | 1215 | 1278 |

SPECIFIC CONDUCTANCES OF $MnCl_2$–$Cu(NO_3)_2$ MIXTURES (M = 2·0)

| Mole ratio $MnCl_2$ : $Cu(NO_3)_2$ | $K \times 10^4$ | $Y \times 10^4$ |
|---|---|---|
| 1/9 | 1263 | 317 |
| 2/8 | 1251 | 587 |
| 3/7 | 1242 | 728 |
| 4/6 | 1237 | 847 |
| 5/5 | 1235 | 890 |
| 6/4 | 1234 | 866 |
| 7/3 | 1236 | 812 |
| 8/2 | 1245 | 625 |
| 9/1 | 1252 | 428 |

The final system studied was the $Fe(NO_3)_3$–KCNS system. The total molar concentration chosen was 0·1 M so the electrical conductivity data could be compared directly with the spectrophotometric data of BABKO.[14] Here (Figs. 7 and 8), the conductance curve shows two extrema, neither of which corresponds to the single extremum obtained spectrophotometrically.

SPECIFIC CONDUCTANCES OF PURE KCNS AND $Fe(NO_3)_3$ SOLUTIONS

| Conc. M/l. | 0·02 | 0·04 | 0·06 | 0·08 | 0·1 |
|---|---|---|---|---|---|
| KCNS; $K \times 10^5$ | 256·3 | 499·4 | 739·0 | 974·3 | 1196·6 |
| $Fe(NO_3)_3$; $K \times 10^5$ | 803·5 | 1417·8 | 2016·5 | 2660·5 | 3011·1 |

It is instructive to compare these results with previous work on the electrical conductivity of mixtures of electrolytes. As early as 1911, BRAY and HUNT[15] found

SPECIFIC CONDUCTANCES OF MIXED KCNS–$Fe(NO_3)_3$ SOLUTIONS

| Mole ratio: KCNS : $Fe(NO_3)_3$ | $K \times 10^5$ | $Y \times 10^5$ |
|---|---|---|
| 5/95 | 2827 | 175 |
| 10/90 | 2682 | 290 |
| 15/85 | 2565 | 370 |
| 20/80 | 2441 | 472 |
| 25/75 | 2324 | 514 |
| 30/70 | 2217 | 542 |
| 35/65 | 2096 | 542 |
| 40/60 | 2028 | 493 |
| 45/55 | 2057 | 383 |
| 50/50 | 1807 | 531 |
| 55/45 | 1730 | 503 |
| 60/40 | 1691 | 455 |
| 65/35 | — | — |
| 70/30 | 1633 | 239 |
| 75/25 | 1627 | 105 |
| 80/20 | 1556 | 29 |
| 85/15 | 1510 | −67 |
| 90/10 | 1414 | −114 |
| 95/5 | — | — |

significant deviations from the mixture rule for the conductivity of solutions containing sodium chloride and hydrochloric acid. SACHANOV[16] found even larger deviations for aqueous solutions containing acetic acid and potassium acetate. In this latter instance, there is, of course, a very significant effect on the ionization of the acetic acid.

[14] A. K. BABKO, *J. Gen. Chem. U.S.S.R.* **16**, 1549 (1946); *Physicochemical Analysis of Complex Compounds in Solution* p. 147. Kiev (1954).
[15] W. C. BRAY and F. L. HUNT, *J. Amer. Chem. Soc.* **33**, 781 (1911).
[16] A. SACHANOV, *Z. Phys. Chem.* **87**, 441 (1914).

Vol. 12 1959/6

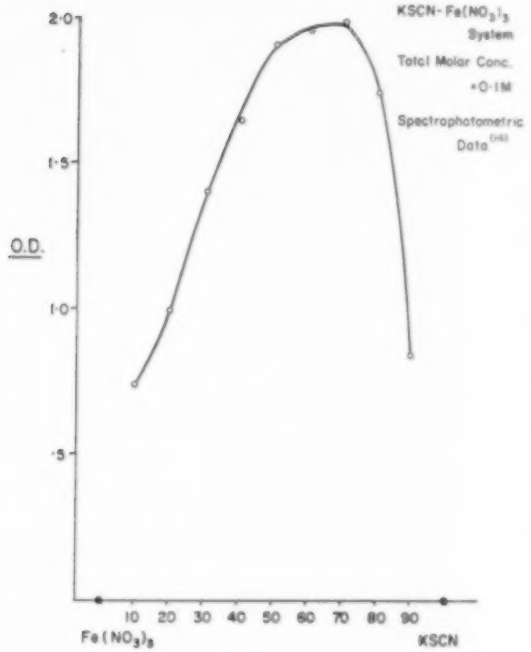



FIG. 7.—Deviation from additivity of optical density in mixtures of KCNS–$Fe(NO_3)_3$.

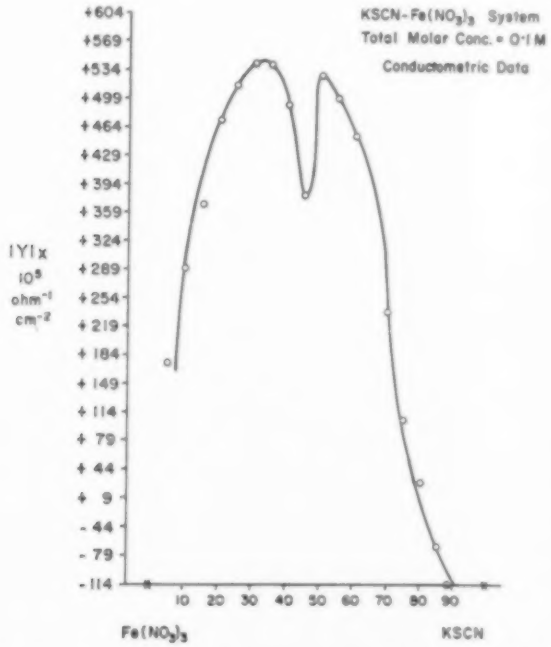



FIG. 8.—Deviation from additivity of specific conductance in mixtures of KCNS–$Fe(NO_3)_3$.

Subsequent investigators[17–29] confirmed and extended these findings. In general, departures from the additivity of conductances are found in practically all kinds of mixtures of simple electrolyte solutions. Even with mixtures of NaCl and KCl solutions, these deviations are of easily measureable magnitude for concentrated solutions. For mixtures of electrolytes of the same charge type, a maximum deviation (negative) is often found in equimolar mixtures. Claims of complex ion formation in such simple systems are not supported by other evidence such as transport number studies.[26,27] In most cases it is even possible to predict the magnitude of the maximum deviation from the properties of the simple salt solutions. VAN RYSSELBERGHE and his co-workers found this maximum deviation to be related to the *difference* of the equivalent conductances of the two salts composing the mixture. The relation for this is[19] $D_{\max} = 0{\cdot}021\Delta\Lambda$, where $D_{\max}$ is the maximum deviation from additivity of the equivalent conductance (almost invariably found in the equimolar mixtures for salts of the same charge type), and $\Delta\Lambda$ is the difference between the equivalent conductances of the two salts.

This breakdown of the mixture rule and of Kohlrausch's law of the independent migration of ions has been studied by ONSAGER and FUOSS[28] and shown by them to be a general characteristic of mixed electrolyte solutions. This feature can be accommodated in our treatment, at least formally by setting up equation (6) as:

$$Y = 10^{-3}\{C_1(\Lambda_{0_1}' - a_1'\sqrt{\mu}) + C_2(\Lambda_{0_2}' - a_2'\sqrt{\mu}) + C_3(\Lambda_{0_3}' - a_3'\sqrt{\mu}) - M(1-x)(\Lambda_{0_1} - a_1\sqrt{\mu}) - Mx(\Lambda_{0_2} - a_2\sqrt{\mu})\} \qquad (11)$$

Here the constants of the equation governing concentration dependence will differ, depending upon whether the electrolyte is in a mixture or a pure solution. When the conditions for an extremum in $Y$ are evaluated anew it is:

(a) found in general not to coincide with a maximum in $C_3$,

(b) to be dependent upon the relative values of the primed and unprimed constants of equation 11, and

(c) capable of occurring in a solution in which no complex is formed at all.

When $dC_3/dx = 0$, and $d\sqrt{(\mu)}/dx = 0$, the expression for $dY/dx$ from equation 11 becomes:

$$\frac{dY}{dx} = M\{(\Lambda_{0_2}' - a_2'\sqrt{\mu}) + (\Lambda_{0_1} - a_1\sqrt{\mu}) - (\Lambda_{0_2} - a_2\sqrt{\mu}) - (\Lambda_{0_1}' - a_1\sqrt{\mu})\} \qquad (12)$$

[17] A. K. SMITH and R. A. GORTNER, *J. Phys. Chem.* **37**, 79 (1933).
[18] A. E. STEARN, *J. Amer. Chem. Soc.* **44**, 670 (1922).
[19] C. W. DAVIES, *J. Chem. Soc.* 448, 2093 (1938).
[20] P. VAN RYSSELBURGHE, S. W. GRINNELL and J. M. CARLSON, *J. Amer. Chem. Soc.* **59**, 336 (1937).
[21] P. VAN RYSSELBERGHE and G. LEE, *J. Amer. Chem. Soc.* **60**, 2776 (1938).
[22] D. J. MEAD and R. M. FUOSS, *J. Phys. Chem.* **49**, 480 (1945).
[23] N. C. C. LI and H. FANG, *J. Chinese Chem. Soc.* **6**, 32, 44 (1938); *Chem. Abstr.* **35**, 5019 (1941).
[24] P. VAN RYSSELBERGHE and L. NUTTING, *J. Amer. Chem. Soc.* **56**, 1435 (1934); **59**, 333 (1937); **55**, 990, 996 (1933).
[25] K. A. KRIEGER and M. KILPATRICK, *J. Amer. Chem. Soc.* **59**, 1878 (1937).
[26] J. DEWEY, *J. Amer. Chem. Soc.* **47**, 1927 (1925).
[27] D. A. MACINNES, *J. Amer. Chem. Soc.* **47**, 1922 (1925).
[28] L. ONSAGER and R. M. FUOSS, *J. Phys. Chem.* **36**, 2689 (1932).
[29] A. N. CAMPBELL, E. M. KARTZMARK and A. G. SHERWOOD, *Canad. J. Chem.* **36**, 1325 (1958).

Vol. 12 1959/6

This leads to the expectation of extrema in systems of constant ionic strength which have no relation to the formation of any complex in the system. This kind of extrema appears to have been found in many of the cases cited above.

As may be inferred from the above discussion, the use of electrical conductivity with Job's method can lead to the postulation of complexes in practically any system examined. Unfortunately such conclusions are generally unwarranted and are usually not supported by studies of the same systems with other methods. The same kinds of difficulties may be expected to occur in studies using high frequency oscillometry with Job's method.[30]

*Acknowledgement*—This work was supported by a Fredrick Gardner Cottrell Grant from the Research Corporation and by AEC Contract No. AT-(40-1)-(1327).

[30] S. S. Cooper and R. J. Spahl, Abstracts of Papers presented at the American Chemical Society meeting in San Francisco (1958). American Chemical Society, Washington, D.C.

Vol.
12
9/60

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 252 to 254. Pergamon Press Ltd. Printed in Northern Ireland

# INITIAL REACTION RATES FROM DTA

H. J. BORCHARDT
General Engineering Laboratory, General Electric Company, Schenectady, New York

(*Received* 23 *February*; *in final form* 15 *May* 1959)

**Abstract**—It is shown that initial reaction rates can be determined in a very simple manner from differential thermal analysis measurements.

IN previous communications[1,2] the utility of obtaining initial reaction rates from DTA was demonstrated. The manner in which this rate can be calculated is described below.

The method is based on the kinetic analysis of DTA curves described by DANIELS and this writer.[3] The equation which relates the reaction rate to quantities obtained from the DTA trace is as follows (equation (7), ref. 3):

$$-\frac{dn}{dt} = \frac{n_0}{KA}\left[C_p \frac{d\,\Delta T}{dt} + K\,\Delta T\right] \tag{1}$$

It was found experimentally that $C_p \dfrac{d\,\Delta T}{dt}$ is small compared to $K\,\Delta T$; therefore dropping the smaller term and cancelling gives

$$-\frac{dn/n_0}{dt} = \frac{\Delta T}{A} \tag{2}$$

where $-\dfrac{dn/n_0}{dt}$ is the rate of reaction (in fraction converted per unit time) at the time (temperature) where the height of the DTA peak is $\Delta T$. $A$ is the total peak area. If it is assumed that the DTA peak can be approximated by a triangle of height $\Delta T_{max}$ and base $\tau$, then $A = \frac{1}{2}\tau\,\Delta T_{max}$ and

$$-\frac{dn/n_0}{dt} = \frac{2\,\Delta T}{\tau\,\Delta T_{max}} \tag{3}$$

By using equation (3) at temperatures where $\Delta T/\Delta T_{max}$ is a small fraction, initial reaction rates can be calculated.

In order to determine the extent to which equation (3) is applicable, $MgCO_3$, $CaCO_3$ (calcite) and kaolinite were subject to differential thermal analysis and initial reaction rates calculated. For comparison, the initial rate of decomposition of these materials was measured by means of conventional weight loss methods.

## EXPERIMENTAL

### A. *Apparatus*

The DTA apparatus is a commercial unit manufactured by the Robert L. Stone Company, Austin, Texas. Weight loss measurements were performed on a Chevenard recording thermobalance. The average particle size of the materials was measured on a Fisher sub-sieve sizer.

[1] H. J. BORCHARDT, *J. Inorg. Nucl. Chem.* **12**, 133 (1959).
[2] H. J. BORCHARDT, *J. Amer. Chem. Soc.* **81**, 1529 (1959).
[3] H. J. BORCHARDT and F. DANIELS, *J. Amer. Chem. Soc.* **78**, 41 (1957).



Vol. 12 1959/6

B. *Materials*

$MgCO_3$, "California Magnesite" from Wards Natural Science Establishment, particle size 2·5 $\mu$; $CaCO_3$, Fisher reagent grade, 6·3 $\mu$; kaolinite, Southern Clays, Incorporated, 1·6 $\mu$.

C. *Procedures*

The DTA measurements in each case were performed in static air with temperature rising at the rate of 12°C/min. The samples were contained in a cylindrical well, open at the top, $\frac{1}{4}$ in. diameter and $\frac{1}{2}$ in. deep. The samples were loosely packed, the packing densities being 33·6, 8·27 and 23·7 per cent of theoretical density respectively for $MgCO_3$, $CaCO_3$, and kaolinite. Weight loss measurements were performed under conditions resembling as close as possible those in the DTA measurements. A small Inconel cylinder was constructed having the same internal dimensions as the DTA sample well. The samples were packed in this cylinder to the same densities as for DTA. The cylinder containing the sample was then inserted into the furnace for the weight-loss measurement.

## RESULTS AND DISCUSSION

The DTA patterns are shown in Fig. 1. The temperatures at which $\Delta T/\Delta T_{max}$ is 0·1 (a small fraction) were determined from the DTA trace and the initial reaction

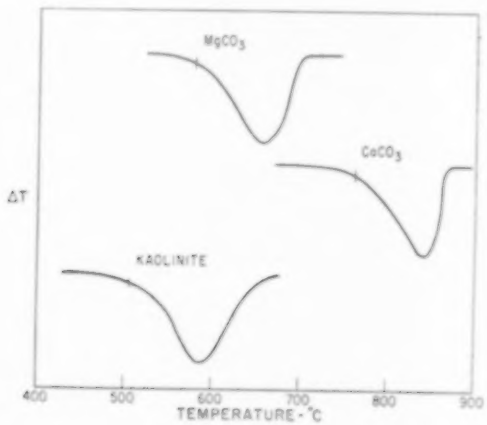



FIG. 1.—DTA patterns of magnesite, calcite, kaolinite. The marker on the curve indicates the point where $\Delta T = 0{\cdot}1\Delta T_{max}$.

rates at these temperatures were calculated from equation (3). These data are listed in Table 1, under the heading "DTA temperature" and "Calculated rate", respectively. The weight loss measurements were made at nearly the same temperatures as those at which the rate is calculated from DTA (actual temperature given in parentheses).

TABLE 1

| DTA temperature (°C) | | Calculated rate (%/min) | Observed rate (%/min) |
|---|---|---|---|
| $MgCO_3$ | 579 | 1·67 | 1·90 (580) |
| $CaCO_3$ | 762 | 2·11 | 2·78 (759) |
| Kaolinite | 506 | 1·29 | 1·28 (506) |

The initial reaction rate is determined from the initial slope of the weight-loss curve. These data are tabulated under "Observed rate". The rates are in units of per cent conversion per minute.

The data indicate that use of equation (3) yields results which are reliable within approximately 20 per cent.

In order to determine the temperature at which the initial reaction rate is 1 per cent conversion per minute, this value is substituted for $-\frac{dn/n_0}{dt}$ and the temperature at which the equality, $0{\cdot}005\tau = \Delta T/\Delta T_{max}$ is satisfied, is determined from the DTA trace.

Per cent conversion per minute as a unit of rate is an extensive quantity and is dependent upon the total effective surface area. For reactions where each powder particle is reacting independently (in contrast to the situation where the powder assemblage is behaving as one large particle[4]) per cent conversion per minute can be translated into a unit which is independent of surface area or particle size as follows:

Consider one of the reactant powders to be composed of spheres of initial volume $V_0$. After some reaction occurs, the volume has been reduced to $V$ and the fraction of original reactant present is $V/V_0$. Since $V = \frac{4}{3}\pi r^3$

$$\frac{dV/V_0}{dt} = \frac{3r^2}{r_0^3}\frac{dr}{dt} \tag{4}$$

By restricting equation (4) to initial reaction rates, $r \cong r_0$, and

$$\frac{dV/V_0}{dt} = \frac{3}{r_0}\frac{dr}{dt} \tag{5}$$

If differences in density between reactant and product are neglected, $dr/dt$ may be considered to be the initial rate of growth of the product layer. The unit of rate, $dr/dt$ is independent of particle size. For particles 6 $\mu$ in diameter, a rate of 1 % per minute is seen to correspond to $dr/dt = 10^{-6}$ cm/min. The various restricting assumptions in the above are rather obvious, and clearly indicate that the figure of $10^{-6}$ cm/min should be considered to be no more than an order of magnitude guide.

[4] For example H. T. S. BRITTON, S. J. GREGG and G. W. WINSOR, *Trans. Faraday Soc.* **48**, 63 (1952).

Vol.
12
1959/6

J. Inorg. Nucl. Chem. 1960, Vol. 12, pp. 255 to 258. Pergamon Press Ltd. Printed in Northern Ireland

# "ONIUM" BASE BOROHYDRIDES—I

## TRIMETHYL SULPHONIUM BOROHYDRIDE

H. G. HEAL
Chemistry Department, Queen's University, Belfast

(*Received* 7 *May* 1959)

**Abstract**—The new compound trimethyl sulphonium borohydride has been prepared. It decomposes above 90° to methane and the co-ordination compound dimethyl sulphide-borine.

BANUS *et al.*[1] have described the preparation of three quaternary ammonium borohydrides. They are stable substances. Even ammonium borohydride itself, which is, as expected, relatively unstable, has been isolated in crystalline form.[2] These observations suggest that many borohydrides of organic "onium" bases, especially the strong fully alkylated or arylated bases, should be easy to make. Apart from those just mentioned, none have been reported, though some tetraphenylborates of "onium" bases are described in the literature.[3,4,5]

The thermal decomposition of "onium" borohydrides is interesting as a possible route to the co-ordination compounds of $BH_3$ with phosphines, thioethers, etc. Some reactions of this type are known, e.g.

$$[(CH_3)_4N]^+[BH_4]^- \xrightarrow[-250^\circ]{150^\circ} CH_4 + (CH_3)_3N{:}BH_3 \qquad (1)$$

Decomposition at higher temperatures, or in presence of catalysts,[6] might be expected in certain cases to yield cyclic boron compounds containing the central atom of the cation in the ring, as in the known reaction

$$3[NH_4]^+[BH_4]^- \rightarrow B_3N_3H_6 + 9H_2 \qquad (2)$$

The investigation reported here is the first of a series with the object of making representative new "onium" borohydrides, and studying their thermal decomposition.

### EXPERIMENTAL METHODS AND RESULTS

The previously unreported compound trimethyl sulphonium borohydride was obtained by the reaction

$$[(CH_3)_3S]^+F^- + Na^+[BH_4]^- \rightarrow NaF\downarrow + [(CH_3)_3S]^+[BH_4]^-$$

in water or ethanol solution. Sodium fluoride is less soluble in ethanol than in water, so that the reaction goes more nearly to completion in ethanol, but this advantage is outweighed by the fact that

[1] M. D. BANUS, R. W. BRAGDON and T. R. P. GIBB, *J. Amer. Chem. Soc.* **74**, 2346 (1952).
[2] R. W. PARRY, D. R. SCHULTZ and P. R. GIRARDOT, *J. Amer. Chem. Soc.* **80**, 1 (1958).
[3] G. WITTIG and P. RAFF, *Liebigs Ann.* **573**, 195 (1951).
[4] G. A. RAZUVAYEV and T. G. BRILKINA, *Dokl. Akad. Nauk SSSR* **85**, 815 (1952).
[5] L. C. HOWICK and R. T. PFLAUM, *Anal. Chim. Acta.* **19**, 342 (1958).
[6] H. J. EMELEUS and G. J. VIDELA, *Proc. Chem. Soc.* 288 (1957); *J. Chem. Soc.* 1306 (1959).

the sodium fluoride precipitated from ethanol is gummy and hard to filter, whereas that from water is crystalline. The following procedure worked well:

Starting with dimethyl sulphide and methyl iodide, trimethyl sulphonium iodide (5·7 g, 28 millimoles) was made[7] and converted by treatment with silver oxide and water to a solution of the base. The base was added to 26·6 milliequivalents of hydrofluoric acid. The excess base made the solution alkaline, which helped to prevent the decomposition of borohydride ion. The solution was concentrated to 4 ml by evaporation at room temperature in a vacuum desiccator. Commercial sodium borohydride was assayed for $BH_4^-$ by the iodate method.[8] A quantity of it containing 28 millimoles of $BH_4^-$ was dissolved in the minimum of water. One drop of the solution was added to the trimethyl sulphonium fluoride solution. This completed the precipitation of traces of silver left in the solution from the silver oxide treatment; it was thought advisable to remove this silver in case it catalytically decomposed the borohydride in the final stages of preparation. The solution was filtered, filtrate and washings totalling 8 ml. The remaining sodium borohydride solution was added, at 17°C. Without filtering off the precipitated sodium fluoride, the mixture was evaporated to dryness over conc. sulphuric acid in a vacuum desiccator, which was continuously exhausted by a rotary pump to remove some gas evolved from the mixture. The residue was extracted at 25°C with three portions of absolute ethanol, totalling 18 ml. This was filtered, and the filtrate cooled to −10°C. Most of the trimethyl sulphonium borohydride crystallized out. It was filtered by suction on a sintered glass crucible, washed quickly with two small portions of cold ethanol, and transferred in the crucible to a desiccator containing sulphuric acid, which was immediately evacuated. The dry product weighed 1·3 g (50 per cent yield). Its identity was confirmed by an I.R. spectrum, taken by the KBr disk method with a Perkin–Elmer Model 21 Spectrometer. The spectrum was almost identical with the superposed spectra of $(CH_3)_3SI$ and $NaBH_4$. Analysis for $BH_4^-$ by the iodate method[8] and the gasometric method[9] showed that it contained 98·5 per cent of the theoretical amount of this ion. Found: C, 38·0; H, 13·9; Calc. C, 39·1; H, 14·3%).

Trimethyl sulphonium borohydride is a light, white, well crystallized solid. It can be kept for long periods if dry, though it always smells of dimethyl sulphide, perhaps owing to slow decomposition by the reaction about to be described. It is very hygroscopic and very soluble in water. It is easily soluble in ethanol, with a large temperature coefficient of solubility, and is easily recrystallized from that solvent, without much decomposition, if the temperature is kept below 25°C.

Samples obtained from several preparations in water solution, and one from a preparation in ethanol (subsequently recrystallized from ethanol) all contained between 98 and 100 per cent of the theoretical amount of borohydride ion.

When heated quickly in a melting capillary, the substance melted at 120°–124°C, with decomposition. Larger samples, heated more slowly *in vacuo*, decomposed suddenly at temperatures from 90°C upwards. A sample of 0·6 g exploded mildly at about 90°. The products of thermal decomposition were investigated as follows. Samples weighing 0·3–0·7 g were placed in an L-shaped tube fitting by means of a ground joint into a reaction vessel, which in turn communicated by wide tubing with a large trap. With the system coupled to the vacuum line and evacuated, the trap was cooled in liquid nitrogen and the reaction vessel heated to 110°. By rotating the L-tube on its ground joint, the sample was dropped in small portions into the reaction vessel, allowing each portion to decompose before adding the next. The chief decomposition products were *methane* and the *compound* $(CH_3)_2S{:}BH_3$. The methane was identified by means of its infra-red spectrum (taken at 93 mm pressure in a 10 cm gas cell), which was identical with the published spectrum of methane.[10] On cooling

[7] H. J. EMELEUS and H. G. HEAL, *J. Chem. Soc.* 1126 (1946).
[8] D. A. LYTTLE, E. H. JENSEN and W. A. STRUCK, *Analyt. Chem.* **24**, 1843, (1952).
[9] W. D. DAVIS, L. S. MASON and G. STEGEMAN, *J. Amer. Chem. Soc.* **71**, 2775 (1949).
[10] *Catalogue of Infra-red Spectral Data of the American Petroleum Institute* (1956).

Vol. 12 1959/6

to the temperature of liquid nitrogen, its pressure fell to about 15 mm, slightly higher than the published vapour pressure of methane (10 mm) perhaps because of the presence of a little hydrogen. The other product, which condensed entirely in the cold trap during preparation, was a colourless liquid at room temperature. It was identified as the known compound $(CH_3)_2S{:}BH_3$[11] by the following evidence.

(a) Its I.R. spectrum in the vapour state was identical with that of a specimen of $(CH_3)_2S{:}BH_3$ made up by mixing $(CH_3)_2S$ and $B_2H_6$ in the mole ratio 2 : 1. The spectrum showed all the stronger bands of $(CH_3)_2S$ and $B_2H_6$, since the compound is largely dissociated in the vapour:[11] in addition, there were strong, narrow bands peaking at 1102 $cm^{-1}$ and 2420 $cm^{-1}$, which must be attributed to the compound itself.

(b) The vapour pressures agreed approximately with those given for $(CH_3)_2S{:}BH_3$ by BURG and WAGNER.[11]

| Temperature °C | Our product | $(CH_3)_2S{:}BH_3$ |
|---|---|---|
| 23·0 | 21·4 mm | 19·5 mm |
| 13·0 | 11·4 | 10·5 |
| 6·5 | 6·7 | 6·8 |

(c) The vapour density indicated a mean molecular weight of 58 at 15° and 10 mm pressure. This figure agrees approximately with the published value[11] and implies considerable dissociation in the vapour.

Our product, however, melted at −27°, whereas BURG and WAGNER reported −38; for $(CH_3)_2S{:}BH_3$.[11]

Measurement of the volume of methane evolved and the weight of $(CH_3)_2S{:}BH_3$ formed showed that the decomposition had gone mainly (apparently over 90 per cent) according to the equation

$$[(CH_3)_3S]^+[BH_4]^- \rightarrow CH_4 + (CH_3)_2S{:}BH_3$$

though an exact material balance was not attempted, in view of the tendency of particles of the starting material to get blown out of the reaction vessel by the violence of the decomposition.

A small quantity of white solid, infusible up to 340°C and soluble in water, was left behind in the reaction vessel. Its I.R. spectrum resembled published spectra of sodium borates.[12]

## DISCUSSION

The ease of preparation and stability of trimethyl sulphonium borohydride lead to the expectation that many other "onium" borohydrides will be made. Its decomposition by elimination of methane parallels the reported modes of decomposition of ammonium borohydride, the substituted ammonium borohydrides, and the

[11] A. B. BURG and R. I. WAGNER, *J. Amer. Chem. Soc.* **76**, 3307 (1954).
[12] F. A. MILLER and C. H. WILKINS, *Analyt. Chem.* **24**, 1253, (1952).

tetraphenyl borates, and probably takes place via a nucleophilic displacement of dimethyl sulphide from the cation by the anion.

$$BH_4^- + CH_3^+ \ldots\ldots S(CH_3)_2 \rightarrow BH_3 + CH_4 + S(CH_3)_2$$

followed by

$$BH_3 + S(CH_3)_2 \rightarrow (CH_3)_2S{:}BH_3$$

However, there is no way of knowing, from our work, to what extent diborane may be formed as an intermediate, subsequently reacting with the dimethyl sulphide.

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 259 to 265. Pergamon Press Ltd. Printed in Northern Ireland

# OBSERVATIONS ON THE RARE EARTHS—LXXI*

## CHEMICAL AND ELECTROCHEMICAL STUDIES OF IODIDE SYSTEMS IN ANHYDROUS N:N′-DIMETHYLFORMAMIDE

T. MOELLER and V. GALASYN
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(*Received* 17 *February* 1959)

**Abstract**—Solvated rare-earth metal iodides having the general formula $LnI_3 \cdot 8DMF$ (Ln = La, Pr, Nd, Sm, or Gd; DMF = N:N′-dimethylformamide) have been prepared by reaction of the hydrated acetate with acetyl iodide in dimethylformamide or by metathesis between the anhydrous chloride and potassium iodide in the same solvent. Several properties of the crystalline salts have been determined. The solvates dissolve readily in N:N′-dimethylformamide, giving solutions exhibiting weak electrolyte behaviour. Such solutions yield amalgams on electrolysis, but conclusive evidence for the deposition of the metals on solid cathodes has not been obtained.

Although the rare-earth metals are conveniently obtained by either metallothermic reduction or electrolytic reduction of certain fused salts, electrodeposition from either aqueous or non-aqueous solutions at ordinary temperatures has been notably successful only when mercury cathodes have been employed.[1–7] In earlier reports from this laboratory,[8–10] however, it has been shown that a number of anhydrous rare-earth metal salts yield conducting solutions in anhydrous ethylenediamine, which give cathodic deposits containing at least small quantities of the metals.

It has been of interest, therefore, to extend these investigations to solvents of high dielectric constant and high fluidity where basicity is still sufficiently high to provide potential stability for the free metals. Such a solvent is N:N′-dimethylformamide. This substance combines high solvent power for a variety of inorganic compounds[11] with a moderately large dielectric constant (36·71 at 25°C)[12] and a fairly low viscosity (0·802 centipoise at 25°C). Many solutes give highly conducting solutions in this solvent,[13–14] but electrodeposition studies have not been extensive.[15]

In the light of preliminary studies which showed that anhydrous lanthanum

* For part LXX, see T. MOELLER and E. P. HORWITZ. *J. Inorg. Nucl. Chem.* **12**, 49 (1959).

[1] L. F. AUDRIETH, E. E. JUKKOLA and R. E. MEINTS with B. S. HOPKINS, *J. Amer. Chem. Soc.* **53**, 1805 (1931).
[2] R. E. MEINTS, B. S. HOPKINS and L. F. AUDRIETH, *Z. Anorg. Chem.* **211**, 237 (1933).
[3] B. S. HOPKINS and L. F. AUDRIETH, *Trans. Electrochem. Soc.* **66**, 135 (1934).
[4] E. E. JUKKOLA with L. F. AUDRIETH and B. S. HOPKINS, *J. Amer. Chem. Soc.* **56**, 303 (1934).
[5] E. E. JUKKOLA, L. F. AUDRIETH and B. S. HOPKINS, *Inorganic Syntheses* **1**, 15 (1939).
[6] E. I. ONSTOTT, *J. Amer. Chem. Soc.* **77**, 2129 (1955).
[7] E. I. ONSTOTT, *J. Amer. Chem. Soc.* **78**, 2070 (1956).
[8] T. MOELLER and P. A. ZIMMERMAN, *J. Amer. Chem. Soc.* **75**, 3940 (1953).
[9] T. MOELLER and P. A. ZIMMERMAN, *Science* **120**, 539 (1954).
[10] T. MOELLER and G. W. CULLEN, *J. Inorg. Nucl. Chem.* **10**, 148 (1959).
[11] *Dimethylformamide*. Product Information Bulletin. E. I. duPont de Nemours and Company, Wilmington, Del. (1953).
[12] G. R. LEADER and J. F. GORMLEY, *J. Amer. Chem. Soc.* **73**, 5731 (1951).
[13] D. P. AMES and P. G. SEARS, *J. Phys. Chem.* **59**, 16 (1955).
[14] P. G. SEARS, E. D. WILHOIT and L. R. DAWSON, *J. Phys. Chem.* **59**, 373 (1955).
[15] A. L. HANSON, D. FROKJER and D. MITCHELL, *Metal Finishing* **49**, No. 4, 48 (1951).

bromide and nitrate are extremely soluble in anhydrous N:N′-dimethylformamide (251·2 and >447 g/l. at 30°C, respectively) but that the strongly oxidizing anode products liberated on electrolysis interfered with cathodic reduction,[16] it was felt that the anhydrous iodides would combine excellent solubility characteristics with a minimum of interference from anode products during electrolytic studies. To this end, the synthesis of anhydrous, but solvated, iodides and the conductance and electrolysis behaviours of such solutes in N:N′-dimethylformamide have been investigated.

## EXPERIMENTAL

*Materials, apparatus and techniques.* Commercially available N:N′-dimethylformamide was dried by the method of LEADER and GORMLEY[12] during the early stages of this study. However, the procedure of THOMAS and ROCHOW[17] was found to be much more effective and was employed during the later stages. Final drying after removal of the benzene–water azeotrope was effected with barium oxide. The lowest specific conductance of solvent dried in this manner was $3{\cdot}7 \times 10^{-7}$ mho $cm^{-1}$ at 25°C. It is of interest that the solvated iodides described below are at least as effective as desiccants as barium oxide.

Rare-earth metal oxides of 99·9+ per cent purity were obtained either from the Lindsay Chemical Division of the American Potash and Chemical Company or from the University of Illinois stocks.

Much of the apparatus employed was that previously described.[10,16] The techniques were generally similar. All solubility and conductance measurements were made at 25 ± 0·025°C. A single-barrier electrolysis cell was adapted for magnetic stirring by means of a small well at the bottom of the cathode compartment. A commercially available* rubber suction bulb permitted accurate pipetting in the dry box, and a static eliminator† reduced mechanical losses during transfer of solids. X-ray powder patterns were obtained with a 114·59 cm (diameter) Norelco camera.

*Preparation of iodides. Acetyl iodide procedure.* WATT *et al.*[18] have obtained various anhydrous halides by treating the appropriate hydrated acetates with acetyl halides in benzene but have reported no quantitative data for iodides. Extension of their procedure to the synthesis of rare-earth metal iodides gave only highly impure products. However, reaction with acetyl iodide in N:N′-dimethylformamide yielded solvated iodides, as

$$Ln(C_2H_3O_2)_3{\cdot}xH_2O + (3 + x)\,CH_3COI \xrightarrow{DMF} LnI_3{\cdot}8DMF + 3(CH_3CO)_2O + xHC_2H_3O_2 + xHI$$

For such reactions, acetyl iodide prepared by the method of THIELE and HAAKH[19] was suitable. Hydrated rare-earth metal acetates were obtained by the procedure of BILTZ and BILTZ.[20] In a typical preparation, 5 g of the appropriate acetate was slurried with 100 ml of N:N′-dimethylformamide in a 500 ml round-bottomed flask. A two-fold excess of freshly prepared acetyl iodide was added in several small portions. Excessive pressure build-up was avoided by momentarily loosening the stopper several times. These operations were carried out in an open hood, care being taken to keep the flask stoppered as much as possible. The resulting clear, brown solution was cooled to room temperature by brief immersion in a dry ice–acetone bath. Then, 50 ml of anhydrous diethyl ether was added in several portions, with vigorous agitation and cooling in the dry ice–acetone bath. The brown crystalline solid produced was washed with ether by decantation. The washed solid was dissolved in a minimum of DMF, and crystallization by addition of ether was repeated. Alternate dissolution and precipitation were carried out until crystalline products free from brown contamination resulted. The final products were washed thoroughly with ether and dried *in vacuo*. Yields varied from 75 to 95 per cent. The first two or three precipitations with ether were usually hampered by separation of two liquid layers. Continued vigorous agitation and cooling effected crystallization.

* "Propipette". Instrumentation Associates, New York, N.Y.

† "Reco Neutra-stat, Model B". Eberbach and Son Co., Ann Arbor, Mich.

[16] G. W. CULLEN. Doctoral Dissertation, University of Illinois (1956).

[17] A. B. THOMAS and E. G. ROCHOW, *J. Amer. Chem. Soc.* **79**, 1843 (1957).

[18] G. W. WATT, P. S. GENTILE and E. P. HELVENSTON, *J. Amer. Chem. Soc.* **77**, 2752 (1955).

[19] J. THIELE and H. HAAKH, *Liebigs Ann.* **369**, 131 (1909).

[20] H. BILTZ and W. BILTZ, *Laboratory Methods of Inorganic Chemistry* (2nd Ed.), p. 245. John Wiley, New York (1928).

Vol. 12 1959/6

*Preparation of iodides. Metathesis procedure.* The small solubility of potassium chloride and the large solubility of potassium iodide in N:N′-dimethylformamide[11] permit metathetical reactions of the type

$$LnCl_3 \text{ (soln.)} + 3KI \text{ (soln.)} \xrightarrow{DMF} LnI_3 \text{ (soln.)} + 3KCl \text{ (solid)}$$

In a typical synthesis, 5 g of neodymium chloride 6-hydrate was added to 150 ml of the dimethylformamide. Then 150 ml of benzene was added, and the benzene–water azeotrope was removed by distillation.[17] Continued distillation removed excess benzene and left a solution of anhydrous neodymium chloride in the dimethylformamide. This solution was then cooled and treated with a stoicheiometric quantity of potassium iodide in the solvent. The resulting suspension was digested under a reflux condenser carrying a drying tube and then filtered in the dry box. The solvated iodide, $NdI_3 \cdot 8DMF$, was recovered by addition of ether, and the small quantity of remaining potassium chloride was removed by dissolving in dimethylformamide, filtering off the residual potassium chloride, and reprecipitating with ether. The yield was 89 per cent.

*Analytical procedures.* The rare-earth metal content of the solvated iodides was determined by a modification of the ethylenediaminetetraacetic acid titration procedure[21] using temperatures of 60–70°C to improve the end point. Iodide was determined by the Volhard method, and carbon, hydrogen, and nitrogen by the usual microanalytical techniques. Analyses for rare-earth metals in electrolysis operations were effected either by titration or by oxalate precipitation.

## RESULTS AND DISCUSSION

*Solvated iodides.* Analytical data summarized in Table 1 indicate compositions very close to $LnI_3 \cdot 8DMF$ in all instances. Although results for the neodymium compound show that the two procedures give identical products, the possible presence of potassium salts in the sample prepared by metathesis precluded its use for conductance studies.

The crystalline solvates are extremely hygroscopic and must be handled in the dry box. They dissolve readily in anhydrous N:N′-dimethylformamide, but traces of water in the solvent yield gelatinous, partially hydrolysed, insoluble products. Solubilities, as determined by analysis of aliquots after equilbration at 25 ± 0·025°C, are summarized in Table 2 and Fig. 1. A discontinuity is apparent at praseodymium. The colours were those of the cations present.

Well-defined X-ray diffraction patterns could not be obtained because of decomposition of the samples even upon only very short exposure to the X-ray beam. Even the poorly defined patterns obtained suggest isomorphism in the series.

*Conductance studies.* Conductance data for the anhydrous systems are summarized in Table 3 and Fig. 2. It is apparent that in the series from lanthanum through gadolinium conductance in the more concentrated solutions decreases with decreasing crystal radii. It is probable that the smaller cations move more slowly through the solution under applied potential because of greater solvation. As expected, these differences are less noticeable in the more dilute regions where all the salts become nearly alike. The conductance behaviour is that of a weak electrolyte in each instance.

Comparison of these conductance values with those previously reported[8,10] indicates the iodides to be stronger electrolytes in N;N′-dimethylformamide than the bromides or nitrates in ethylenediamine or monoethanolamine.

*Electrolysis studies.* These were limited to lanthanum and neodymium iodide solutions as typical. In no instance with platinum foil, platinum gauze or copper foil cathodes was there conclusive evidence for deposition of the metal. Gassing around the cathode was common. In a single electrolysis using lanthanum iodide

[21] G. SCHWARZENBACH, *Die Komplexometrische Titration* p. 68. F. Enke, Stuttgart (1956).

TABLE 1.—PROPERTIES OF $LnI_3 \cdot 8DMF$-TYPE SALTS

| Symbol | Analytical data | | | | Melting point (sealed tube) (°C) |
|---|---|---|---|---|---|
| | Calculated for $LnI_3 \cdot 8DMF$ | | Found | | |
| | (%) | Atom ratio | (%) | Atom ratio | |
| La | 12·57 | 1 | 12·45 | 1·00 | 73·0–75·0 |
| I | 34·48 | 3 | 33·88 | 2·98 | |
| C | 26·10 | 24 | 26·16 | 24·3 | |
| H | 5·11 | 56 | 5·22 | 57·6 | |
| N | 10·15 | 8 | 10·29 | 8·20 | |
| O* | 11·59 | 8 | 12·00 | 8·37 | |
| Pr | 12·74 | 1 | 12·86 | 1·00 | 90·5–92·5 |
| I | 34·41 | 3 | 34·36 | 2·96 | |
| C | 26·05 | 24 | 25·90 | 23·7 | |
| H | 5·10 | 56 | 5·03 | 54·7 | |
| N | 10·13 | 8 | 9·91 | 7·75 | |
| O* | 11·57 | 8 | 11·94 | 8·17 | |
| Nd | 13·00 | 1 | 12·95 | 1·00 | 91·5–94·5 |
| I | 34·31 | 3 | 34·38 | 3·01 | |
| C | 25·97 | 24 | 26·21 | 24·3 | |
| H | 5·09 | 56 | 5·14 | 56·8 | |
| N | 10·10 | 8 | 9·83 | 7·82 | |
| O* | 11·53 | 8 | 11·49 | 8·00 | |
| Nd† | 13·00 | 1 | 12·89 | 1·00 | |
| I | 34·31 | 3 | 34·61 | 3·05 | |
| C | 25·97 | 24 | 26·02 | 24·3 | |
| H | 5·09 | 56 | 5·07 | 56·3 | |
| N | 10·10 | 8 | 9·99 | 7·98 | |
| O* | 11·53 | 8 | 11·42 | 7·99 | |
| Sm | 13·48 | 1 | 13·49 | 1·00 | 97·5–100·0 |
| I | 34·12 | 3 | 33·80 | 2·97 | |
| C | 25·83 | 24 | 25·89 | 24·0 | |
| H | 5·06 | 56 | 5·08 | 56·3 | |
| N | 10·04 | 8 | 10·06 | 8·02 | |
| O* | 11·47 | 8 | 11·68 | 8·14 | |
| Gd | 13·98 | 1 | 14·01 | 1·00 | 102·0–104·0 |
| I | 33·92 | 3 | 33·91 | 2·99 | |
| C | 25·68 | 24 | 25·46 | 23·7 | |
| H | 5·03 | 56 | 4·96 | 55·1 | |
| N | 9·99 | 8 | 9·62 | 7·69 | |
| O* | 11·40 | 8 | 12·04 | 8·43 | |

* Oxygen calculated by difference.
† Prepared by metathesis. All other samples by acetyl iodide procedure.

Vol. 12 1959/60

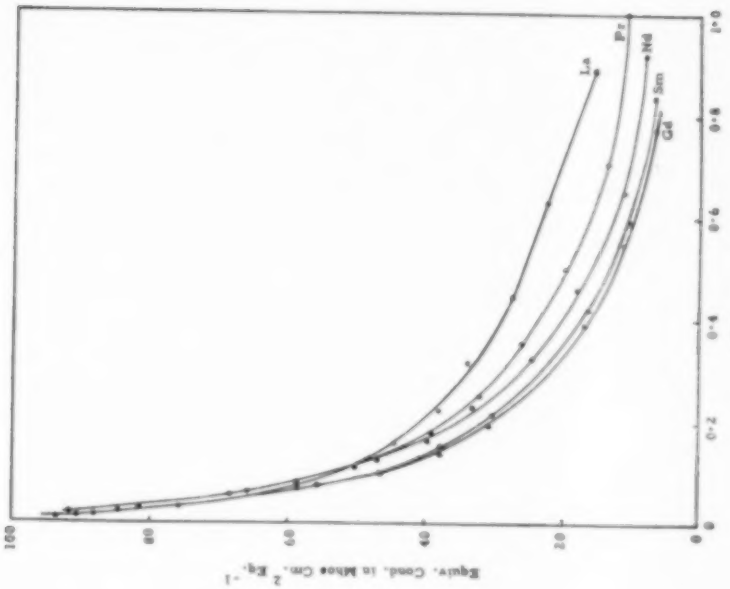



Fig. 2.—Conductance of DMF solutions of $LnI_3$ at 25°C.

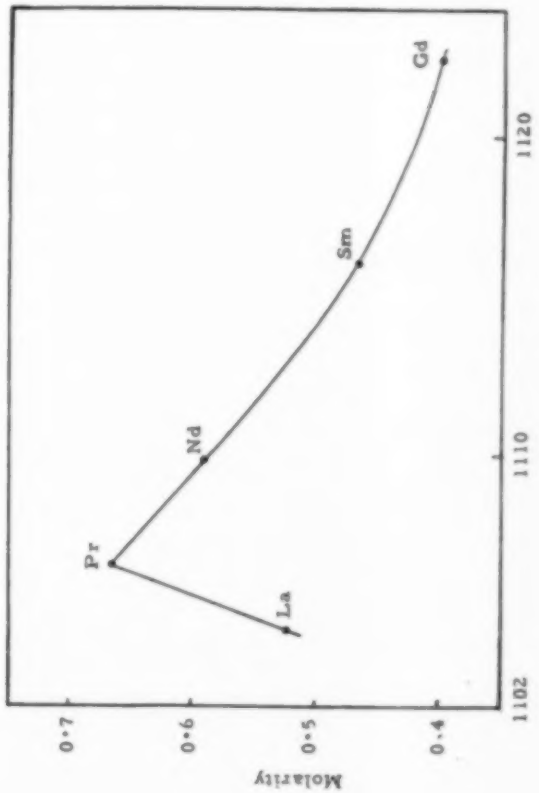



Fig. 1.—Solubilities of $LnI_3 \cdot 8$ DMF in anhydrous DMF at 25°C.

at an initial current density of 1·1 mA/cm² under a potential of 25 V, a black deposit, accompanied by gassing, hissing and sparking, appeared at localized spots on the platinum foil cathode. Rotation of the cathode caused uniform deposition over its surface. Simultaneously, the catholyte became dark in colour and developed the pungent odour of solvent decomposition. Analyses showed that some 38 per cent

TABLE 2.—SOLUBILITY DATA AT 25 ± 0·025°C

| Compound | Solubility | |
|---|---|---|
| | (g/l.) | (g mole/l.) |
| $LaI_3$·8DMF | 578·7 | 0·5240 |
| $PrI_3$·8DMF | 735·8 | 0·6650 |
| $NdI_3$·8DMF | 657·1 | 0·5921 |
| $SmI_3$·8DMF | 520·7 | 0·4666 |
| $GdI_3$·8DMF | 451·0 | 0·4018 |

of the lanthanum originally present in the catholyte had been removed and that the cathode deposit contained 63·04 per cent lanthanum, 4·23 per cent carbon, 0·74 per cent hydrogen, and 1·32 per cent nitrogen. The black deposit was unreactive toward the atmosphere but reacted vigorously with either hydrochloric acid or nitric acid. In each instance, a small quantity of black residue remained. Only a few faint diffraction lines could be seen on a powder pattern. Heat treatment *in vacuo*

TABLE 3.—CONDUCTANCE DATA FOR IODIDE SOLUTIONS AT 25 ± 0·025°C

| $LaI_3$·8DMF | | $PrI_3$·8DMF | | $NdI_3$·8DMF | | $SmI_3$·8DMF | | $GdI_3$·8DMF | |
|---|---|---|---|---|---|---|---|---|---|
| N* ×10³ | Λ† mho cm² equiv⁻¹ | N ×10³ | Λ mho cm² equiv⁻¹ | N ×10³ | Λ mho cm² equiv⁻¹ | N ×10³ | Λ mho cm² equiv⁻¹ | N ×10³ | Λ mho cm² equiv⁻¹ |
| 788 | 15·75 | 999 | 10·61 | 843 | 8·03 | 700 | 6·66 | 603 | 6·87 |
| 394 | 22·27 | 500 | 13·57 | 422 | 11·06 | 350 | 10·66 | 301 | 11·25 |
| 197 | 27·43 | 250 | 19·61 | 211 | 17·69 | 175 | 16·40 | 151 | 17·05 |
| 98·4 | 33·84 | 125 | 25·96 | 105 | 24·38 | 87·5 | 21·83 | 75·4 | 24·67 |
| 49·2 | 38·21 | 62·4 | 32·21 | 52·7 | 33·21 | 43·7 | 30·43 | 37·7 | 30·77 |
| 24·6 | 44·54 | 31·2 | 39·10 | 26·3 | 39·54 | 21·9 | 37·81 | 18·8 | 37·77 |
| 12·3 | 50·08 | 15·6 | 46·80 | 13·2 | 49·77 | 10·9 | 45·60 | 9·42 | 46·50 |
| 6·15 | 56·91 | 7·80 | 55·90 | 6·59 | 58·73 | 5·46 | 55·49 | 4·71 | 58·60 |
| 3·08 | 65·91 | 3·90 | 65·90 | 3·29 | 67·78 | 2·73 | 65·93 | 2·35 | 68·09 |
| 1·54 | 73·38 | 1·95 | 73·85 | 1·65 | 74·55 | 1·37 | 75·18 | 1·18 | 75·76 |
| 0·77 | 78·93 | 0·98 | 81·66 | 0·82 | 84·33 | 0·68 | 84·63 | 0·59 | 82·00 |
| 0·39 | 87·01 | 0·49 | 91·80 | 0·41 | 89·54 | 0·34 | 91·46 | 0·29 | 88·10 |
| 0·19 | 90·63 | 0·24 | 93·85 | 0·21 | 94·17 | 0·17 | 93·57 | 0·15 | 90·48 |

* N = normality
† Λ = equivalent conductance

at 1000°C for 1½ hr, effected no visible agglomeration or fusion. However, a larger number of illdefined diffraction lines resulted. Comparison with patterns for lanthanum and its oxide showed a number of lines common to both metal and oxide patterns but also a number characteristic of neither. It is probable that some metal was deposited but that contamination with organic material was excessive. However, a similar deposit was not obtained in any other experiment.

Vol. 12 1959/60

White, non-adherent cathode deposits resulted in many instances. These solids contained rare earth (ca. 50 per cent by weight), reacted with acids and were not hygroscopic. They were amorphous to X-ray. Heat treatment evolved condensible vapours (probably solvent) and yielded black solids giving poorly defined and uncharacterizable powder patterns. These deposits were larger with lanthanum than with neodymium. Stirring had no effect.

Darkening of the catholyte and production of amine-like odours indicate electrolytic decomposition of the solvent. Electrolysis of N:N′-dimethylformamide with lead electrodes is said to effect ca. 52·7 per cent reduction of the material.[22,23] The anolyte remained unchanged. Liberated iodine did not diffuse into the cathode compartment.

Neodymium amalgams resulted with a stirred mercury-pool cathode. A typical 7½ hr electrolysis with an initial current of 100 mA at 20 V yielded a liquid amalgam containing 0·86 per cent neodymium. Removal of neodymium from the catholyte was essentially complete. The neodymium content of the anolyte decreased from 0·1878 M to 0·1703 M. Solvent decomposition and precipitation of a gray solid were noted in the cathode compartment. Formation of the latter also characterized electrolytic preparation of the amalgam in ethanol.[24] Neodymium amalgams develop voluminous oxide coatings on exposure to moist air and react readily with dilute acids.

*Acknowledgement*—The authors are indebted to the Air Force Office of Scientific Research for the financial support that rendered this investigation possible. The work was done under Contract FA 18(600)–1535.

[22] N. I. Gavrilov and A. V. Kopérina, *J. Gen. Chem.* (*U.S.S.R.*) **9**, 1394 (1939).
[23] N. I. Gavrilov, A. V. Kopérina and M. M. Klutcharova, *Bull. Soc. Chim. Fr.* **12**, 773 (1945).
[24] E. E. Jukkola. Doctoral Dissertation, University of Illinois (1933).

ol.
12
9/60

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 266 to 275. Pergamon Press Ltd. Printed in Northern Ireland

# AN EXAMINATION OF THE BASIC NATURE OF THE TRIHALIDES OF PHOSPHORUS, ARSENIC AND ANTIMONY*†

R. R. HOLMES‡

Departments of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania and Purdue University, Lafayette, Indiana

(*Received* 25 *March* 1959)

**Abstract**—Literature reports of the complexes, $PCl_3$-$BF_3$ and $PCl_3$-$BCl_3$, were investigated by conducting vapour pressure-composition measurements on the systems at low temperatures. Large, positive deviations from ideal liquid behaviour were observed in both cases, indicating no tendency for complex formation. An examination of the properties of $POCl_3$-$BCl_3$ indicates the complexes reported in the literature to be phosphorus oxychloride–boron trihalide addition compounds. The 1 : 1 addition complexes of boron tribromide with phosphorus trichloride and tribromide were prepared, thus confirming the existence of these complexes. The $PCl_3$-$BBr_3$ complex was noted to exchange on standing. The $AsCl_3$-$BCl_3$ system was studied and found to be analogous to the $PCl_3$-$BF_3$ system. Examination of the $PCl_3$-$Al_2Cl_6$, $PCl_3$-$Ga_2Cl_6$, $AsCl_3$-$Al_2Cl_6$, $AsCl_3$-$Ga_2Cl_6$, $SbCl_3$-$BCl_3$, $AsBr_3$-$BBr_3$ and $SbBr_3$-$BBr_3$, systems failed to give any evidence for the formation of stable complexes. Thus, of the halides studied only phosphorus trichloride and tribromide exhibited basic tendencies. The donor tendencies of the trihalides of phosphorus are discussed.

Vol. 12 1959/6

IT is known that the trimethyl derivatives[1] as well as hydrides of phosphorus, arsenic and antimony[2,3] exhibit basic properties in reactions with typical electron pair acceptor molecules.

In connexion with the trichloride derivatives, 1 : 1 complexes of phosphorus trichloride with boron trifluoride,[4] boron trichloride[5] and boron tribromide[6] have been reported. In these phosphorus trichloride is believed to act as an electron pair donor.§ There exists also a report of a 1 : 1 complex between phosphorus tribromide and boron tribromide.[9] In the case of arsenic trichloride and antimony trichloride no complexes with the boron trihalides are known.

To ascertain more fully the relative donor tendencies of the trihalides of phosphorus, arsenic and antimony the phosphorus trihalide–boron trihalide complexes

* Abstracted in part from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The remainder of the work was conducted at Carnegie Institute of Technology.

† Presented in part before the Physical and Inorganic Division at the 129th Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

‡ Research fellow (1951–1953) on a grant from the Atomic Energy Commission for the study of "Chemistry of Polyvalent Metal Halides."

§ The 1 : 1 complex, $PCl_3$ . $TiCl_4$, has been shown by GROENEVELD *et al.*[7] to be actually $POCl_3$ . $TiCl_4$. The compound, $F_3P$ . $BH_3$, probably has special bonding in view of the non-existence of $F_3P$ . $BF_3$.[8]

[1] R. H. HARRIS. Ph.D. Thesis, Purdue University (1952).
[2] N. SIDGWICK, *The Chemical Elements and Their Compounds* Vol. 1, pp. 761 and 797. Clarendon Press, Oxford (1950).
[3] E. FLETCHER. Ph.D. Thesis, Purdue University (1952).
[4] P. BAUMGARTEN and W. BRUNS, *Ber. Dtsch. Chem. Ges.* **80**, 517 (1947).
[5] A. STIEBER, *C.R. Acad. Sci., Paris* **195**, 610 (1932).
[6] E. WIBERG and K. SHUSTER, *Z. Anorg. Chem.* **213**, 94 (1933).
[7] W. L. GROENEVELD, J. W. SPRONSEN and H. W. KOUWENHOVEN, *Rec. Trav. Chim.* **72**, 950 (1953).
[8] A. B. BURG and G. BRENDEL, *J. Amer. Chim. Soc.* **80**, 3198 (1958).
[9] J. TARIBLE, *C.R. Acad. Sci., Paris* **116**, 1521 (1893).

reported in the literature were reinvestigated. The studies were extended to the investigation of the trichlorides and tribromides of arsenic and antimony with boron trichloride and boron tribromide. Attempts were also made to form complexes by interacting the trichlorides of phosphorus and arsenic with aluminium and gallium trichlorides.

## RESULTS AND DISCUSSION

### *Phosphorus trichloride–boron trifluoride*

The results (Table 1) of the vapour pressure–composition measurements made on the solution of gaseous boron trifluoride in liquid phosphorus trichloride at −78·5° show the gas to be very insoluble. The Henry's law constant was calculated to be

TABLE 1.—THE PHOSPHORUS TRICHLORIDE-BORON TRIFLUORIDE SYSTEM AT −78·5°

| $P_{BF_3}$ (exptl) (mm) | Mole fraction $BF_3$ | $P_{BF_3}$ (calc.)* (mm) |
|---|---|---|
| 63·2 | 0·0054 | 14·0 |
| 220·5 | 0·014 | 36·3 |
| 318·1 | 0·024 | 62·2 |
| 440·0 | 0·033 | 85·5 |
| 490·8 | 0·035 | 90·7 |

* Calculated pressures using Raoult's law. A value of 3·41 atm was used for the vapour pressure of pure boron trifluoride.[10]

$1{\cdot}3 \times 10^4$ mm. There is noted a linear variation of pressure with increasing mole fraction of boron trifluoride. Furthermore, when these results are compared with those expected for ideal liquid behaviour (column 3 of Table 1), large, positive deviations are observed. Thus, the evidence points to the nonexistence of any stable complex.

The result obtained in this study is in marked contrast to observations made by BAUMGARTEN and BRUNS.[4] They claimed to have isolated a 1 : 1 addition complex of phosphorus trichloride and boron trifluoride from petroleum ether at −12°. The substance was reported to be a white crystalline solid which began to decompose at −6°.

### *Phosphorus trichloride–boron trichloride*

No apparent reaction was observed on treating phosphorus trichloride with boron trichloride in vacuum at dry ice temperatures, as evidenced by the complete recovery of the volatile component, boron trichloride.

Further measurements were made on the system by studying the pressure–composition diagrams at 25·4° and −45·0°.

Table 2 lists the results obtained at 25·4° where both components were entirely in the gaseous phase. On comparing columns 1 and 3, close agreement between the experimental pressures and those calculated from Dalton's law is observed, showing that no interaction took place.

[10] H. S. BOOTH and D. R. MARTIN, *Boron Trifluoride and Its Derivatives*. John Wiley, New York (1949).

Table 3 lists the data on the pressure of boron trichloride gas over liquid phosphorus trichloride at −45·0°. The pressure varies linearly with increasing mole fraction of boron trichloride. Slight positive deviations from ideal liquid behaviour are observed on comparing columns 1 and 3. As in the gaseous study, the data on the liquid clearly show that no tendency for association or complex formation exists.

TABLE 2.—THE PHOSPHORUS TRICHLORIDE–BORON TRICHLORIDE SYSTEM AT 25·4°

| Total press. (exptl) (mm) | Mole ratio $BCl_3/PCl_3$ | Total press. (calc.)* (mm) |
|---|---|---|
| 72·49 | 0·0 | 72·49 |
| 84·76 | 0·170 | 84·7 |
| 92·85 | 0·282 | 92·9 |
| 102·5 | 0·399 | 101·3 |
| 111·5 | 0·527 | 110·5 |
| 121·5 | 0·663 | 120·4 |
| 136·0 | 0·861 | 134·6 |
| 154·8 | 1·123 | 153·5 |

* Total pressures calculated assuming additivity of the partial pressures of each component.

TABLE 3.—THE PHOSPHORUS TRICHLORIDE–BORON TRICHLORIDE SYSTEM AT −45·0°

| Total press. (exptl) (mm) | Mole fraction $BCl_3$ | Total press. (calc.)* (mm) |
|---|---|---|
| 7·47 | 0·085 | 6·6 |
| 15·25 | 0·218 | 12·9 |
| 20·29 | 0·309 | 17·3 |
| 24·33 | 0·374 | 20·3 |
| 27·55 | 0·435 | 23·2 |
| 29·79 | 0·481 | 25·4 |
| 32·61 | 0·524 | 27·4 |
| 35·25 | 0·556 | 29·0 |
| 36·84 | 0·593 | 30·7 |

* Pressures calculated from Raoult's law, $P_{calcd} = P^{\circ}_{BCl_3}N_{BCl_3} + P^{\circ}_{PCl_3}(1 - N_{BCl_3})$. A value of 50·0 mm was used for the vapour pressure of pure boron trichloride ($P^{\circ}_{BCl_3}$)[11] and a value of 2·5 mm for the vapour pressure of pure phosphorus trichloride ($P^{\circ}_{PCl_3}$) at −45·0°.

Again the results are not in accord with the literature. STIEBER[5] claimed that by mixing liquid boron trichloride and phosphorus trichloride at temperatures between room temperature and −80°, a 1 : 1 complex formed on removing the excess reactant by evaporation *in vacuo*. The product was a white, crystalline solid, readily sublimable and decomposed by water or alkalies.

[11] A. STOCK and O. PRIESS, *Ber. Dtsch. Chem. Ges.* **47**, 3109 (1914).

Vol. 12 1959/6

*Phosphorus oxychloride–boron trichloride*

When phosphorus trichloride, which had not been purified too carefully, was mixed with boron trichloride in vacuum at −45°, a small amount of white needles precipitated from the liquid mixture. The needles possessed properties similar to the ones reported by STIEBER.[5] They were easily sublimable at room temperature and readily hydrolysed by water.

This substance was felt to be a result of a reaction of boron trichloride with an impurity in phosphorus trichloride. It is known that phosphorus trichloride absorbs oxygen readily from the air forming phosphorus oxychloride.[12] The latter substance

TABLE 4.—SATURATION PRESSURE DATA FOR PHOSPHORUS OXYCHLORIDE–BORON TRICHLORIDE AND THE UNKNOWN SOLID

| $Cl_3PO : BCl_3$ | | Unknown solid | |
|---|---|---|---|
| Press. (mm) | Temp. (°C) | Press. (mm) | Temp. (°C) |
| 4·0 | 0·0 | 4·8 | 0·0 |
| 6·1 | 5·6 | 9·4 | 9·7 |
| 9·2 | 10·1 | 14·1 | 14·8 |
| 20·6 | 20·0 | 20·7 | 19·6 |
| 33·9 | 26·4 | 29·9 | 24·2 |
| | | 30·0 | 24·4 |
| | | 44·2 | 29·5 |
| | | 67·1 | 35·1 |

was thought to be impurity. To check this, a known sample of $Cl_3PO$-$BCl_3$ was prepared by direct interaction of the components in the vacuum system. The saturation vapour pressures were obtained at a series of temperatures and compared with similar measurements made on the unknown solid. The results are summarized in Table 4 and plotted in Fig. 1. The points fall on the same straight line, thus identifying the unknown solid as the addition compound, $Cl_3PO$-$BCl_3$.

*Reaction of phosphorus trichloride and tribromide with boron tribromide.* On treating boron tribromide with phosphorus trichloride at 0°, the solid addition product, $PCl_3$-$BBr_3$, formed as reported by WIBERG and SHUSTER[6]. On standing in vacuum for three days, the solid changed to a colourless liquid as reported,[6] and in doing so, a gas was evolved. WIBERG and SHUSTER made no mention concerning the appearance of a gas. The gas was identified as boron trichloride and the liquid as phosphorus tribromide.

The compound, $PBr_3$-$BBr_3$, prepared by TARIBLE[9] who reported it as a white solid, melting at 61°, was confirmed. It melted at 61–62° and remained unchanged on standing in vacuum.

[12] N. SIDGWICK, *The Chemical Elements and Their Compounds* Vol. 1, p. 753. Clarendon Press, Oxford (1950).

*Arsenic trichloride–boron trichloride*

Pressure-composition measurements were made at 0° on the solution of boron trichloride in liquid arsenic trichloride. The results are summarized in Table 5 and plotted in Fig. 2. The figure shows that no reaction has occurred; moreover, the system exhibits large positive deviations from ideal behaviour.

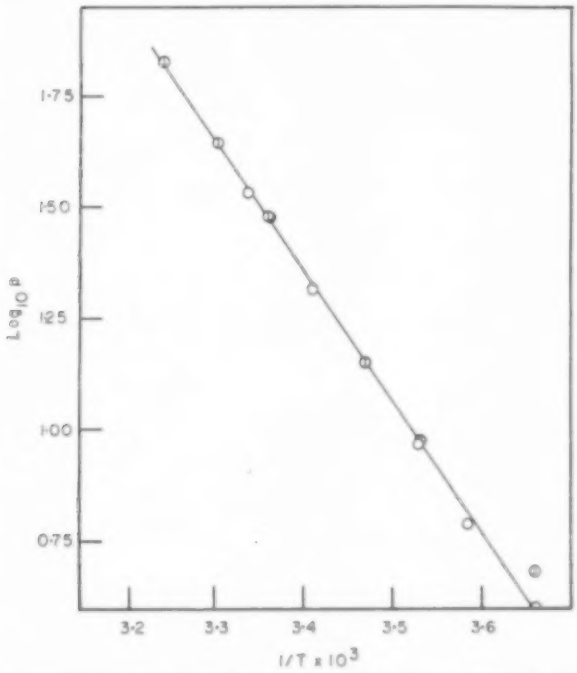



FIG. 1.—Temperature variation of the dissociation pressures of phosphorus oxychloride–boron trichloride, —○—; and the unknown solid, —①—.

*Arsenic tribromide–boron tribromide and antimony tribromide–boron tribromide*

Arsenic tribromide dissolves in boron tribromide at room temperature with the absorption of heat giving a colourless solution. The solubility at 0° estimated from vapour pressure lowering data assuming ideal solution behaviour is 30 g of arsenic tribromide per 100 g of boron tribromide. The pressure composition diagram at 0° showed no indication for formation of a complex. Table 6 summarizes the data. In the experiment, 1·40 mmoles of arsenic tribromide was used.

Antimony tribromide (1·73 mmoles) and boron tribromide (3·77 mmoles) were brought together in the special ampoule, sealed and allowed to remain in contact for several hours. The antimony tribromide appeared insoluble at room temperature, but on heating, a miscible system formed. On cooling solid separated out. This process was repeated. Analysis of the volatile products showed no reaction had occurred. Complete recovery of the boron tribromide (3·77 mmoles) was effected.

In a further experiment boron tribromide was added to a solution of antimony tribromide in carbon disulphide at room temperature. No reaction was observed to take place.

Vol.
12
1959/6

TABLE 5.—THE ARSENIC TRICHLORIDE–BORON TRICHLORIDE SYSTEM AT 0°

| Exptl. press. (mm) | Mole fraction $BCl_3$ | Calc. press.* (mm) |
|---|---|---|
| 66·2 | 0·030 | 17·7 |
| 120·4 | 0·070 | 36·7 |
| 179·6 | 0·134 | 66·9 |
| 230·4 | 0·216 | 106 |
| 268·7 | 0·301 | 146 |
| 301·5 | 0·373 | 180 |
| 316·5 | 0·426 | 205 |
| 335·9 | 0·498 | 240 |
| 344·8 | 0·547 | 263 |
| 362·2 | 0·585 | 281 |

* Pressures calculated from Raoult's law using the relation, $P_{calcd} = P^{\circ}_{BCl_3}N_{BCl_3} + P^{\circ}_{AsCl_3}N_{AsCl_3}$, where $P^{\circ}_{BCl_3} = 476$ mm and $P^{\circ}_{AsCl_3} = 3{\cdot}5$ mm at 0°.

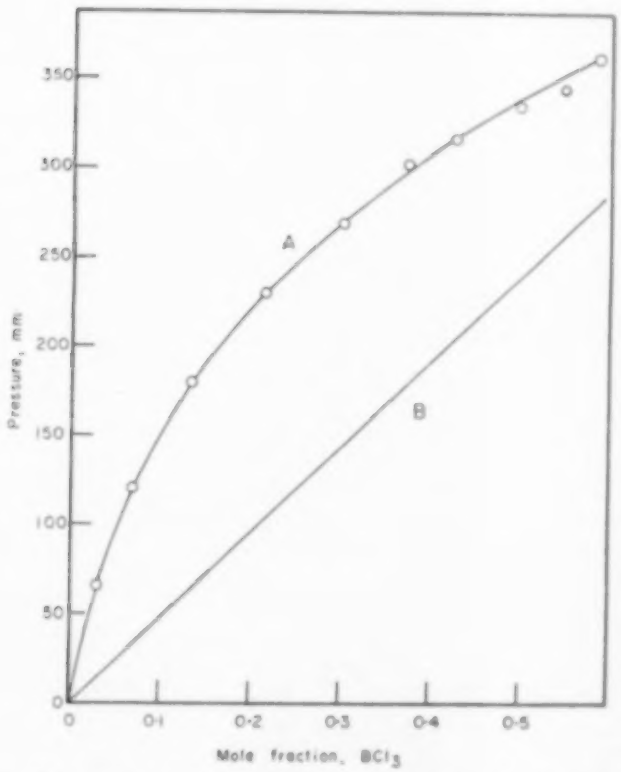



FIG. 2.—The arsenic trichloride–boron trichloride system at 0°; *A*, experimental curve; *B*, Raoult's law.

*Other systems studied*

Attempts were made to form complexes between each of the following pairs of trihalides: $PCl_3$-$Al_2Cl_6$, $PCl_3$-$Ga_2Cl_6$, $AsCl_3$-$Al_2Cl_6$, $AsCl_3$-$Ga_2Cl_6$ and $SbCl_3$-$BCl_3$. The starting components were completely recovered in all cases, showing the lack of reaction leading to the formation of *stable* complexes.[13]

## CONCLUSION

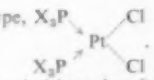
To summarize, literature reports of the existence of the complexes, $Cl_3P$-$BF_3$ and $Cl_3P$-$BCl_3$, were proven erroneous. Using a stronger electron pair acceptor molecule, boron tribromide,[14] the complexes with phosphorus trichloride and

TABLE 6.—THE ARSENIC TRIBROMIDE–BORON TRIBROMIDE SYSTEM AT 0°

| $\frac{n\ BBr_3}{n\ AsBr_3}$ | Press. (mm) |
|---|---|
| 0·04 | 0 |
| 0·11 | 12·9 |
| 0·31 | 13·9 |
| 0·57 | 14·6 |
| 0·81 | 14·5 |
| 1·06 | 14·9 |
| 1·37 | 15·2 |
| 1·53 | 15·2 |
| 1·77 | 15·2 |
| 1·97 | 15·4 |

phosphorus tribromide were verified, the former being unstable with respect to exchange. With other donor molecules, aluminium trichloride and gallium trichloride, no interaction was observed with phosphorus trichloride. Complete lack of any basic tendencies was manifested by the trichlorides and tribromides of arsenic and antimony in the systems studied. Thus only phosphorus trichloride and tribromide show any donor tendencies and the latter are only observable when a strong acceptor molecule is employed. Possibly with the use of stronger acids basic tendencies may be observable with trihalides of arsenic and antimony as well.*

The results obtained in this study are in qualitative agreement with what would be predicted on the basis of electronic interpretations.

* There exists stable complexes of phosphorus trifluoride and trichloride of the type, 

However, the bonds in these compounds are more complicated than the simple electron pair (sigma bond) type discussed here. CHATT[15] has postulated that, in addition to the normal sigma bond, these complexes contain pi bonding formed by electron donation from filled 5*d* levels of platinum.

[13] N. N. GREENWOOD, *J. Inorg. Nucl. Chem.* **8**, 234 (1958) reports slight interaction between $PCl_5$ and $Ga_2Cl_6$. The phase diagram shows an incongruently melting 1 : 1 compound (m.p. 28°) which exhibits no existence in the liquid phase as determined by infra-red data.

[14] H. C. BROWN and R. R. HOLMES, *J. Amer. Chem. Soc.* **78**, 2173 (1956).

[15] J. CHATT, *Nature, Lond.* **165**, 637 (1950).

Vol. 12 1959/6

Phosphorus trichloride is observed to be a much weaker base than the corresponding hydride or alkyl compound. To illustrate more clearly, it is known that the trimethylphosphine–boron trichloride addition compound is dissociated to a negligible extent in the gas phase at 100°.[1] The corresponding phosphine–boron trichloride complex begins to dissociate above 20°;[10] whereas, in the phosphorus trichloride–boron trichloride system, no tendency for association was observed down to Dry Ice temperatures.

Moreover, on changing the central atom from phosphorus to arsenic, basic tendencies decreased as expected, in the line with the increased nuclear charge on the heavier atom.

TABLE 7.—VAPOUR PRESSURES OF THE PURIFIED LIQUID CHLORIDES

| Compound | Press (mm) | Temp. (°C) |
|---|---|---|
| $PCl_3$ | 35·1 | 0·0 |
| $POCl_3$ | 7·7 | 0·0 |
| $AsCl_3$ | 10·0 | 26·0 |

It is interesting to note that both phosphorus trichloride and tribromide possess acceptor properties as well; for example, reacting with trimethylamine to form easily dissociable 1 : 1 adducts.* Thus, it might be said that the phosphorus trihalides are rare examples of amphoteric substances in the Lewis sense, behaving both as weak electron donors and weak electron acceptors.

## EXPERIMENTAL

*Materials.* Boron trifluoride (Matheson) was purified by preparation of the addition compound with anisole, followed by regeneration at higher temperatures. The gas exhibited a vapour pressure of 298 mm at −111·8° with a molecular weight of 68·1 as compared to the calculated value of 67·8.

Boron trichloride (Matheson) was readily purified by regeneration from the nitrobenzene addition compound using a procedure previously reported.[11] The resultant material was tensiometrically homogeneous and exhibited a vapour pressure of 476 mm at 0°.

Boron tribromide was a sample previously prepared by the reaction of bromine with calcium boride and purified by distillation in an all-glass fractionating column, b.p. 90·2° at 748 mm, vapour pressure 19·0 mm at 0°.

Phosphorus trichloride, phosphorus oxychloride and arsenic trichloride were purified in the vacuum system by repeated fractionation of the liquids through appropriately cooled traps. The vapour pressures are given in Table 7.

Phosphorus tribromide (Eastman Kodak), supplied in a sealed ampoule, was used without further purification. It was opened in a dry box just prior to transferring it into the vacuum system.

The trichlorides of aluminium, gallium and antimony were purified by sublimation in vacuum just prior to their use in the reactions studied. The gallium trichloride was part of a sample prepared by the action of hydrogen chloride on gallium metal in an all-glass system at 200°. Aluminium trichloride and antimony trichloride were reagent grades available commercially.

Arsenic tribromide (City Chemical Corp., New York) was used without further purification.

* An elaboration of the thermodynamic properties of complexes of this type and resultant discussion of the nature of the acceptor bond is to be published soon.

[11] D. R. MARTIN, *Chem. Rev.* **34**, 461 (1944).

Antimony tribromide (Fisher Scientific Co.) was purified by sublimation in vacuum just prior to its use in the reaction studied.

*Apparatus.* The pressure-composition studies, performed at or below room temperature, were carried out with a Henry's law apparatus attached to the vacuum system similar to that used previously.[17] The procedure followed was to introduce or remove known increments of the volatile component in a two component system. The pressure in the reaction system was measured after each addition or removal, allowing sufficient time for equilibrium to be established. In this way the diagram was obtained which indicated the extent or lack of interaction.

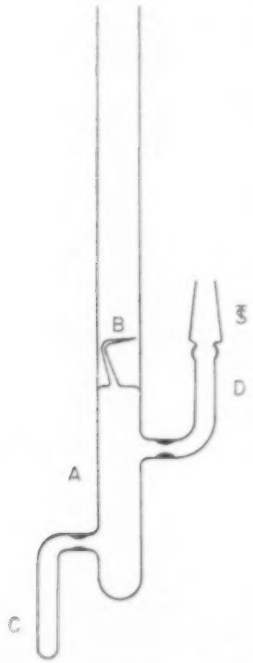



FIG. 3.—Special glass ampoule.

In studying the interaction in systems at temperatures above room temperature, a special glass ampoule was employed (Fig. 3).

In a typical experiment the ampoule was filled with dry nitrogen, weighed and placed in a dry box. A small amount of the nonvolatile component was introduced into section (*C*) and the ampoule reweighed. The ampoule was evacuated and the material in the side arm sublimed into section (*A*). A dry ice cone trapped the sublimate in the ampoule proper. After sublimation the side-arm was sealed off, dry nitrogen admitted and the ampoule and sealed off portion reweighed to obtain the weight of the sublimate. The apparatus was then reevacuated. An excess of the volatile component was measured out and condensed in the ampoule. Arm (*D*) was sealed off. Following this the ampoule and contents were heated to about 100°, generally for approximately one to three hours. Afterwards, if the solid was insoluble in the liquid component, it woud be heated gently to melting with a cool flame to allow for reaction, if any, to take place in the liquid phase. The ampoule was reattached to the vacuum system, opened by dropping a glass-enclosed iron hammer on the break tip (*B*) and the volatile component removed and analysed to ascertain if reaction had occurred.

*Decomposition of phosphorus trichloride–boron tribromide.* The gaseous product from the room temperature decomposition of $PCl_3$–$BBr_3$ was investigated. It was fractionated in vacuum and found

[17] H. C. BROWN, L. P. EDDY and R. WONG, *J. Amer. Chem. Soc.* **75**, 6275 (1953).

Vol. 12 1959/60

to be tensiometrically homogeneous. It exhibited a vapour pressure of 4 mm at −78·5° with a molecular weight of 113, identifying it as boron trichloride (calculated molecular weight is 117). The extent of exchange corresponded to 94 per cent completion in three days as measured by the amount of boron trichloride that was given off. The liquid remaining had a negligible vapour pressure at room temperature. On considering the stoicheiometry involved, it is presumed that the liquid is phosphorus tribromide.

*Acknowledgement*—The author wishes to express his appreciation to Prof. H. C. BROWN for the many helpful discussions during the progress of this work and the preparation of the manuscript.

ol.
12
9/60

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 276 to 280. Pergamon Press Ltd. Printed in Northern Ireland

# THERMAL DECOMPOSITION OF THE HEAVIER RARE-EARTH METAL NITRATE HYDRATES

## THERMOBALANCE AND DIFFERENTIAL THERMAL ANALYSIS STUDIES

W. W. WENDLANDT and J. L. BEAR
Department of Chemistry, Texas Technological College Lubbock, Texas

(*Received* 6 *April* 1959; *in revised form* 25 *May* 1959)

**Abstract**—The thermal decomposition of europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium nitrate 4-hydrates was studied by means of the thermobalance and differential thermal analysis (DTA). The compounds were classified into three groups on the basis of their thermal decomposition patterns: Group A—europium, gadolinium and dysprosium; group B—holmium, erbium and thulium; and group C—ytterbium and lutetium. The DTA endotherms agreed fairly well with the corresponding decomposition reactions found on the weight-loss curves.

ONLY fragmentary information is available in the literature concerning the thermal decomposition of the rare-earth nitrate hydrates. Several early studies have reported the melting points and minimum dehydration temperatures for a number of the metal nitrates.[1] DUTT,[2] by thermal decomposition weight-loss studies as well as conductometric and thermometric titrations, found that intermediate basic nitrates of the composition, $MONO_3$, $M_2O_3 \cdot 2MONO_3$, and $3M_2O_3 \cdot 4N_2O_5$, were obtained. WENDLANDT,[3] using the thermobalance, studied the thermal decomposition of the lighter rare-earth nitrates hydrates, those from lanthanum to samarium. It was found that the metal nitrates, with the exception of cerium and samarium, decomposed according to the general sequence: $M(NO_3)_3 \cdot 6H_2O \rightarrow M(NO_3)_3 \rightarrow MONO_3 \rightarrow$ metal oxide. It is of interest to note that horizontal weight levels corresponding to the anhydrous metal nitrates were found in the thermograms. Cerium nitrate hydrate, as was expected, decomposed directly to $CeO_2$ without the formation of an intermediate basic nitrate while samarium did not give an anhydrous nitrate weight level.

In a continuation of this previous study, the thermal decomposition of the other rare-earth metal nitrate hydrates, those from europium to lutetium (with the exception of terbium) were studied on the thermobalance and also by differential thermal analysis (DTA).

## EXPERIMENTAL

*Thermobalance.* The automatic-recording thermobalance has previously been described.[4] The rare-earth nitrate 4-hydrates were thermally decomposed to the oxides using sample sizes ranging in weight from 80 to 90 mg. Duplicate, and in some cases, triplicate runs were made on each compound. The furnace heating rate was 5·0°C per min. A slow stream of air was passed through the furnace during the pyrolysis run.

[1] J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* Vol. 5, Chap. 38. Longmans, Green, London (1924).
[2] N. K. DUTT, *J. Indian Chem. Soc.* **22**, 97, 107 (1945).
[3] W. W. WENDLANDT, *Anal. Chim. Acta* **15**, 435 (1956).
[4] W. W. WENDLANDT, *Analyt. Chem.* **30**, 56 (1958).



Vol. 12 1959/60

DTA *apparatus*. The apparatus consisted of a Nichrome wound stainless steel tube furnace and sample holder, a motor driven Powerstat to control the furnace heating rate, and a microvolt strip-chart recorder. The differential temperatures in the sample wells were detected with platinum–90 per cent platinum–10 per cent rhodium thermocouples. Sample sizes ranged from 300 to 375 mg. The samples were diluted with about one-third their weight with freshly ignited alumina, using alumina also in the reference thermocouple well. The furnace heating rate was about 10·5°C per min.

*Chemicals*. The rare-earth compounds were obtained in the form of their oxides of 99·9% purity from Research Chemicals, Inc. Burbank, Calif., and the Lindsay Chemical Co., West Chicago, Ill. The purity of the compounds was that listed by the supplier.

*Preparation of the metal nitrate hydrates*. The rare-earth oxides were dissolved in a minimum amount of 6 N $HNO_3$, evaporated to about one-half their initial volumes, and allowed to crystallize in a desiccator over concentrated $H_2SO_4$. In all cases, the rare-earth nitrate 4-hydrates were obtained.

## DISCUSSION

### *Thermobalance studies*

The thermal decomposition curves of the metal nitrates are given in Figs. 1 and 2 with the composition data being given in Table 1.

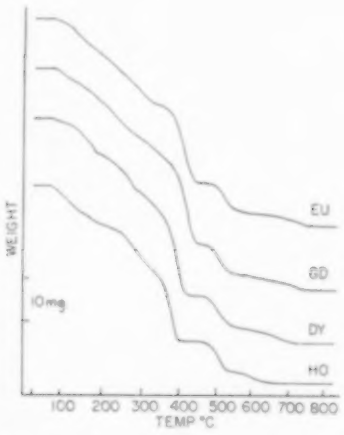



FIG. 1.—Thermobalance weight loss curves for the rare-earth nitrate 4-hydrates.

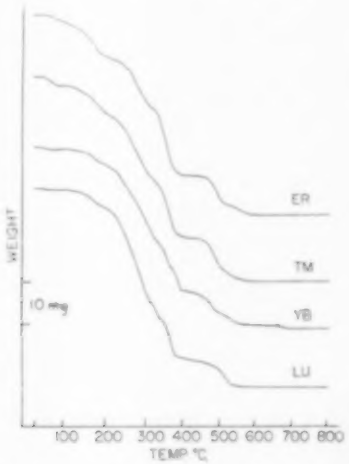



FIG. 2.—Thermobalance weight loss curves for the rare-earth nitrate 4-hydrates.

The amount of hydrate water found in the metal nitrates, with the exception of ytterbium, was not in agreement with a previous study.[5] MARSH found that 5- and 6-hydrates were generally obtained, with a 3·5 and 4-hydrate being reported for ytterbium and at 4·5-hydrate for lutetium. The lower hydrates found in this investigation were probably the more stable compounds formed on desiccation over concentrated $H_2SO_4$.

The general pyrolysis patterns for the metal nitrates can be classified into three main groups. They are: Group A—europium, gadolinium and dysprosium; Group B—holmium, erbium and thulium; and Group C—ytterbium and lutetium.

In Group A, the general pyrolysis pattern consisted of the following sequence: $M(NO_3)_3 \cdot 4H_2O \xrightarrow{I} MONO_3 \xrightarrow{II} M_2O_3$. The minimum decomposition temperatures for step I were from 75° to 80°C, while for step II, they were from 455° to 480°C. The

[5] J. K. MARSH, *J. Chem. Soc.* 561 (1941).

minimum oxide level temperatures were in the 730°–760°C temperature range. It is of interest to note that horizontal weight levels corresponding to the composition, $MONO_3$, were found for europium and dysprosium but not for gadolinium. The $MONO_3$ weight levels were stable over a 50° temperature range at the heating rate employed. The experimental composition data corresponding to the $M_2O_3 \cdot MONO_3$ compounds were probably fortuitous since horizontal weight levels were not obtained.

TABLE 1.—THE THERMAL DECOMPOSITION OF THE RARE-EARTH NITRATE HYDRATES; COMPOSITION DATA

| Rare-earth nitrate hydrate | Oxide (%) | | | | | |
|---|---|---|---|---|---|---|
| | $M(NO_3)_3 \cdot 4H_2O$ | | $MONO_3$ | | Other | |
| | found | calc. | found | calc. | found | calc. |
| Europium | 42·3 | 42·91 | 77·4 | 76·51 | 93·5 | $Eu_2O_3 \cdot EuONO_3$ |
| | 42·4 | | 77·1 | | 92·2(615°C) | 90·72 |
| Gadolinium | 43·2 | 43·59 | 78·3 | 77·00 | 92·7 | $Gd_2O_3 \cdot GdONO_3$ |
| | 43·0 | | 78·2 | (455°C) | 93·2(585°C) | 90·95 |
| Dysprosium | 43·6 | 44·23 | 78·1 | 77·53 | 93·1 | $Dy_2O_3DyONO_3$ |
| | 43·5 | | 78·4 | | 93·3(610°C) | 91·19 |
| Holmium | 44·5 | 44·66 | 77·4 | 77·76 | 53·9 | $Ho(NO_3)_3$ |
| | 44·8 | | 77·3 | | 51·0(245°C) | 53·83 |
| Erbium | 44·4 | 44·96 | 78·9 | 77·97 | | |
| | 44·7 | | 79·1 | | | |
| Thulium | 45·6 | 45·29 | 78·1 | 78·30 | | |
| | 45·3 | | 77·7 | | | |
| Ytterbium | 45·7 | 45·70 | 77·2 | 78·48 | | |
| | 46·0 | | 78·2 | (390°C) | | |
| Lutetium | 47·8 | 47·94 | 82·8(?) | 78·65 | | |
| | 47·1 | | 83·9(?) | (380°C) | | |

It is probable that the composition of the pyrolysis curve would correspond better to a mixture of $MONO_3$ and $M_2O_3$ and not to a stoicheiometric compound.

For Groups B and C, the pyrolysis pattern consisted of essentially the same sequence as for Group A except that the $MONO_3 + M_2O_3$ mixture was missing. For step I, the minimum decomposition temperatures were from 55° to 120°C., while for step II, they were from 380° to 460°C. With the exception of ytterbium, the minimum oxide level temperatures were obtained in the 500°–600°C temperature range. The main difference between Groups B and C was the presence in Group B of definite horizontal weight levels corresponding to the composition, $MONO_3$. The thermal stability of the $MONO_3$ compounds in Group B was similar to those found in Group A.

The experimental composition values found for $MONO_3$ in Group C were probably fortuitous since horizontal weight levels were not obtained. It is probable that the composition of the curve in this region corresponds better to a mixture of $MONO_3$ and $M_2O_3$ rather than to a definite compound.

Vol. 12 1959/60

In general, it should be noted that the metal oxide levels were obtained at increasingly lower temperatures as the atomic weight of the metal ion increased. Another trend which may be attributed to the decreasing basicity of the rare-earths is the absence of the $M(NO_3)_3$ weight level. Such a weight level was found for the lighter rare-earth compounds.[3] The behaviour of the rare-earth nitrates is thus similar, in regards to decreasing basicity of the metal ions, as was found for the rare-earth sulphates[6] and chlorides.[7,8]

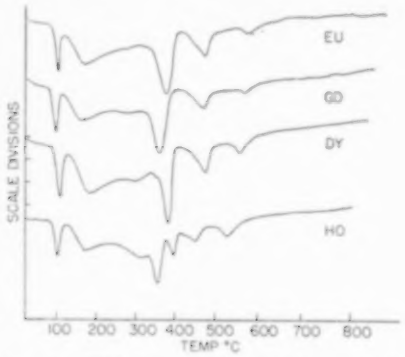



FIG. 3.—DTA thermal decomposition curves for the rare-earth nitrate 4-hydrates.

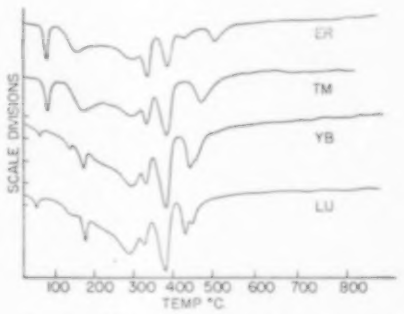



FIG. 4.—DTA thermal decomposition curves for the rare-earth nitrate 4-hydrates.

*Differential thermal analysis studies*

The thermal decomposition curves of the metal nitrate hydrates are given in Figs. 3 and 4. All of the peaks were due to endothermic reactions and will be designated as endotherms. The DTA curves supplement the weight loss curves except that a rigorous comparison cannot be made of the endotherm temperatures because of the different heating rates employed and also the different furnace conditions.

The DTA curves for Group A compounds were all quite similar in appearance. The first endotherms were due to the fusion of the metal nitrate hydrates. This was followed by their gradual dehydration reactions which took place over a 250°–270° temperature range. Because of these gradual dehydration reactions, the endotherms appeared as broad peaks. Before the dehydration was completed, the metal nitrates began to decompose through a series of oxynitrates as shown by the next three small endotherms. The first endotherm maximas occurred in the 365°–385°C temperature range, with the others were at correspondingly higher temperatures. The terminal products in the oxynitrate decompositions were the metal oxides.

As was expected, Group B compounds all gave very similar decomposition curves. The main difference between the Group A and B curves was the splitting of the first metal oxynitrate endotherm into two smaller ones. The reason for this splitting is not known but a possible explanation for it may be found by examining the thermobalance curves for Group B compounds, especially the curve for holmium. Holmium gave two breaks in the curve before the $HoONO_3$ weight level was obtained. The first break, at 245°C, corresponded approximately to the composition for anhydrous

[6] W. W. WENDLANDT, *J. Inorg. Nucl. Chem.* **7**, 51 (1958).
[7] W. W. WENDLANDT, *J. Inorg. Nucl. Chem.* **5**, 118 (1957).
[8] W. W. WENDLANDT, *J. Inorg. Nucl. Chem.* **9**, 136 (1959).

$Ho(NO_3)_3$. The second break, at about 345°C, corresponded to an intermediate compound of unknown composition, somewhere in between $Ho(NO_3)_3$ and $HoONO_3$. This unknown intermediate compound then decomposed to give the $HoONO_3$ level at 405°C.

On the basis of this curve and also the other weight-loss curves in Group B, the splitting of the DTA endotherm could be due to the decomposition of the $M(NO_3)_3$ to an intermediate compound and the subsequent decomposition of this compound to the $MONO_3$. It should be noted that the second endotherm formed during the splitting became larger than the first as the atomic number of the metal increased. Apparently, the heat of reaction becomes much greater for the latter step.

The DTA curves for the Group C compounds were also similar to each other in appearance. The heat of fusion of the metal nitrate hydrates appeared to be much smaller than in the other two groups and was split into two smaller endotherms. The second peak in the splitting of the oxynitrate endotherm of the Group A compounds has now become much larger than the original first peak.

*Acknowledgements*—It is a pleasure to acknowledge R. MANDLE of the Davison Chemical Co., and also the Lindsay Chemical Co., for the samples of thulium and lutetium oxides.

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 281 to 286. Pergamon Press Ltd. Printed in Northern Ireland

# THE SPECIES OF Co(III) PRESENT IN AQUEOUS PERCHLORIC ACID SOLUTIONS

L. H. SUTCLIFFE and J. R. WEBER
Department of Inorganic and Physical Chemistry, The University, Liverpool 7

(*Received* 28 *May* 1959)

**Abstract**—A spectrophotometric study of cobaltic perchlorate solutions has shown that high concentrations and low acidities favour the formation of complex species the intensity of absorption of which in the ultra-violet region is much greater than that of the relatively uncomplexed Co(III) ion. It is suggested that hydrolysis of the latter occurs rapidly and is followed by the slow formation of polynuclear species.

THE instability of perchlorate solutions of cobaltic ion prevents a really precise study being made of the species present. However, the experience gained in this laboratory by working with such solutions has led to an attempt to obtain some semi-quantitative data. In a previous paper[1] the hydrolysis constant of Co(III) was determined and found to be of the same order as that of Fe(III);[2] furthermore, it was consistent with the kinetic data obtained for the effect of acidity on the reaction between Co(III) and Ce(III) ions in perchlorate solutions. The present investigation, while failing to lead to a revised hydrolysis constant, has cast some doubt on the earlier findings.

BAWN and WHITE[3] have explained the kinetics of the decomposition of aqueous cobaltic sulphate in terms of the species $CoOH^{2+}$ and $(Co—O—Co)^{4+}$. Recently, BAXENDALE and WELLS[4] examined the reaction of cobaltic perchlorate with water and interpreted their kinetic results by postulating that Co(III) was present mainly in the dimeric form; if this is true, then the diamagnetism of cobaltic perchlorate solutions[5] can be explained otherwise than by assuming that the ground electronic state of $Co^{3+}{\cdot}6H_2O$ has the configuration $(a_{1g})^2(t_{1u})^6(e_g)^4(t_{2g})^6$. In addition, these workers obtained spectrophotometric evidence for a hydrolysed form. The purpose of the studies described here was to obtain spectrophotometric evidence for polynuclear species of Co(III).

## EXPERIMENTAL

*Materials.* The preparation of cobaltic perchlorate has been described previously.[6] Other reagents were of A.R. quality.

All optical measurements were made with a Unicam S.P. 500 spectrophotometer in which the absorption cells could be maintained at a temperature constant to ±0·02°C. A solution of perchloric acid and sodium perchlorate was added to an aliquot of cobaltic perchlorate solution taken from a stock solution maintained at 0°C. This procedure enabled experiments to be conducted with comparable concentrations of Co(III), as its rate of decomposition is very low at this temperature. Optical density readings at 330 mμ were taken at suitable time intervals and when the absorption reached a

[1] L. H. SUTCLIFFE and J. R. WEBER *Trans. Faraday Soc.* **52**, 1225 (1956).
[2] R. M. MILBURN and W. C. VOSBURGH *J. Amer. Chem. Soc.* **77**, 1352 (1955).
[3] C. E. H. BAWN and A. G. WHITE *J. Chem. Soc.* 331 (1951).
[4] J. H. BAXENDALE and C. F. WELLS *Trans. Faraday Soc.* **53**, 800 (1957).
[5] H. L. FRIEDMAN, J. P. HUNT, R. A. PLANE and H. TAUBE *J. Amer. Chem. Soc.* **73**, 4028 (1951).
[6] G. HARGREAVES and L. H. SUTCLIFFE *Trans. Faraday Soc.* **51**, 786 (1955).

maximum a portion of the solution was analysed volumetrically. For the analysis the Co(III) solution was added to excess Fe(II) and back titrated with standard Ce(IV) solution.

The ionic strength was restricted to the range 1·0 to 1·1 M.

## RESULTS

Preliminary measurements showed that cobaltic perchlorate solutions which had been stored for several days at 0°C became optically unstable (as observed at 330 mμ) when allowed to warm to 20°C, while the chemical composition remained unchanged.

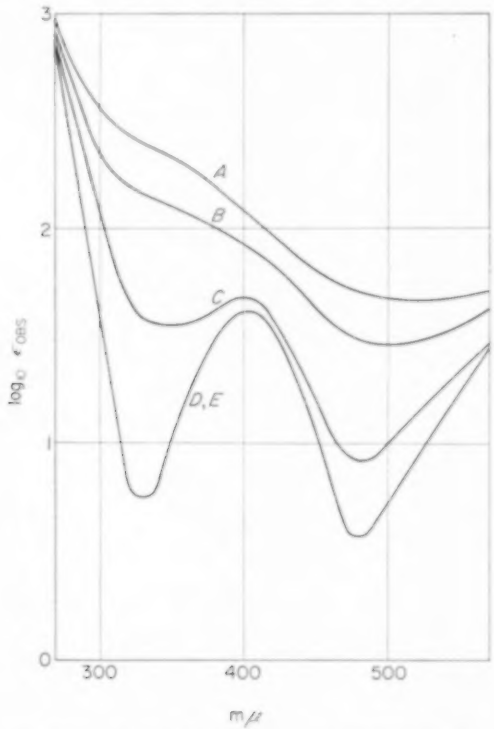



FIG. 1.—Absorption spectra of cobaltic perchlorate solutions at 20·00°C. The respective $[HClO_4]$, [Co(III)], and ionic strengths are: *A*: 0·06 M, $2·3 \times 10^{-3}$ M, 1·0 M; *B*: 0·10 M, $5·2 \times 10^{-3}$ M, 1·0 M; *C*: 0·29 M, $8·0 \times 10^{-3}$ M, 1·0 M; *D*: 1·00 M, $9·4 \times 10^{-3}$ M, 1·0 M; *E*: 4·50 M, $12·8 \times 10^{-3}$ M, 4·5 M.

The optical density was seen to rise slowly to a maximum; calculation of the extinction coefficients showed that the solutions of lower acidity had the higher extinction coefficients. These observations suggested that an equilibrium involving a hydrolysed species of Co(III) was present which was favoured by increasing temperature. Cooling the solutions to 0°C for an hour showed that the equilibrium was not readily reversible.

The extent of the optical changes occurring for various conditions is illustrated in Fig. 1: BAXENDALE and WELLS[4] obtained similar results. Fig. 2 shows how the absorption spectrum is dependent upon the cobaltic perchlorate concentration for a given concentration of perchloric acid. With concentrations of Co(III) as low as $1 \times 10^{-3}$ M, the absorption spectrum was only affected by changes of temperature and acidity; it may be seen from Fig. 3 that the observed molar extinction coefficient

Vol. 12 1959/6

($\varepsilon_{obs}$) at 330 m$\mu$ (which appeared to be the wavelength most sensitive to changes in environment) approaches a constant value of six at the higher acidities. It is our opinion that this value represents the extinction coefficient of $Co^{3+} \cdot 6H_2O$. The data in Fig. 3 enabled a concentration of perchloric acid to be chosen at which hydrolysis is a minimum; the maximum value of ca. 0·35 M is dictated by the need to maintain constant ionic strength. The cobaltic perchlorate concentration was then varied while

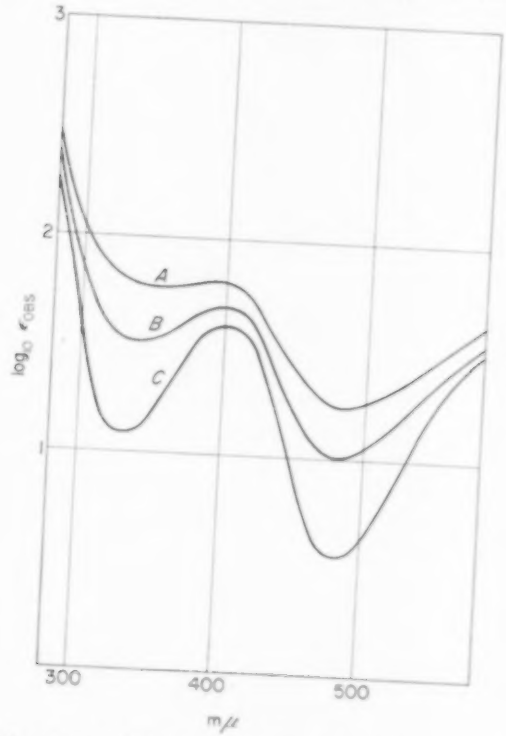



FIG. 2.—Absorption spectra of cobaltic perchlorate solutions at 20·00°C, $[HClO_4] = 0{\cdot}34$ M and ionic strength 1·1 M. The cobaltic perchlorate concentrations are $A = 18{\cdot}6 \times 10^{-4}$ M $B = 9{\cdot}2 \times 10^{-4}$ M, $C = 2{\cdot}5 \times 10^{-3}$ M.

suppressing the hydrolysis as much as possible, with the results shown in Fig. 4. An interesting feature is that the plots converge to a common intercept corresponding to an extinction coefficient of six at 330 m$\mu$. The points enclosed in squares were obtained by allowing the Co(III) solution to reach a given concentration by thermal decomposition rather than by dilution. The remainder of the points correspond approximately to the maximum optical density observed, i.e. when the hydrolysed species had reached an appreciable concentration; an indication of the time intervals required is given in Table 1, which contains all the data presented in Fig. 4. Fig. 5 illustrates the rate data for the measurements made at 28·00°C. The initial fall in optical density is more likely to be due to reaction of Co(III) with impurities rather than to a shift of equilibrium. From Table 1 it can be seen that there is a marked temperature dependence for the time required to reach the maximum extinction

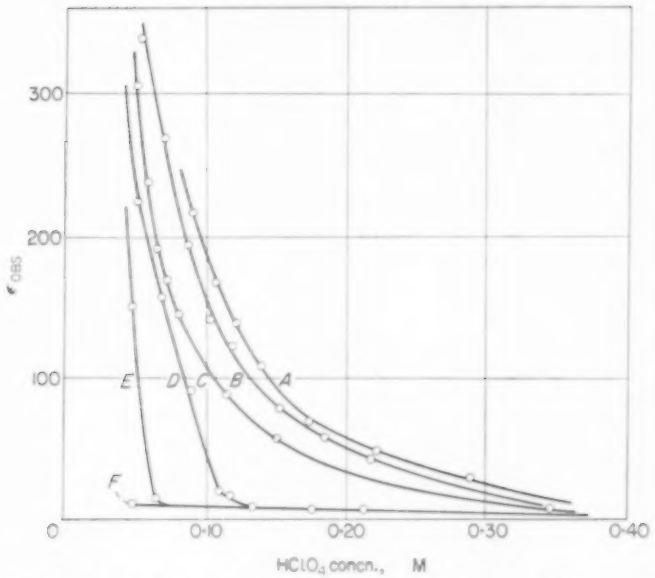



FIG. 3.—Variation of the observed extinction coefficient at 330 mμ with acidity. Temperatures: $A$ = 32·00°C, $B$ = 28·00°C, $C$ = 24·00°C, $D$ = 20·00°C, $E$ = 16·00°C, $F$ = 12·00°C. Ionic strength = 1·0 M. Co(III) concentration $2{\cdot}7 \times 10^{-4}$–$10{\cdot}4 \times 10^{-4}$ M.

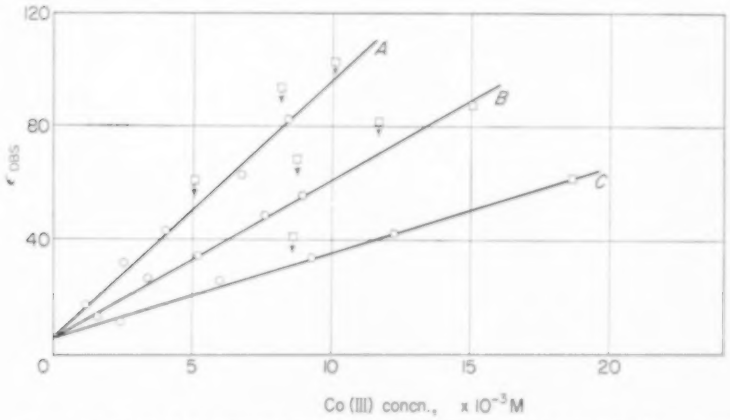



FIG. 4.—Variation of the observed extinction coefficient at 330 mμ with Co(III) concentration at approximately constant acidity. $A$: 32·00°C, $[HClO_4]$ = 0·305 M; $B$: 28·00°C, $[HClO_4]$ = 0·339 M; $C$: 20·00°C, $[HClO_4]$ = 0·330 M. Ionic strength = 1·0–1·1 M. ⊡ denotes a reading obtained from a stock solution which had been allowed to decompose.

coefficient, which suggests that the heat of formation of the complex species is considerable.

All the data presented so far were obtained from stock solutions of Co(III) prepared at 0°C, and in an attempt to gain further insight into the rate processes involved some electrolytic preparations were carried out at 20°C. On examining the resultant cobaltic perchlorate solutions optically at this temperature it was found that the optical density still rose to a maximum value as observed previously. This indicates

Vol. 12 1959/6

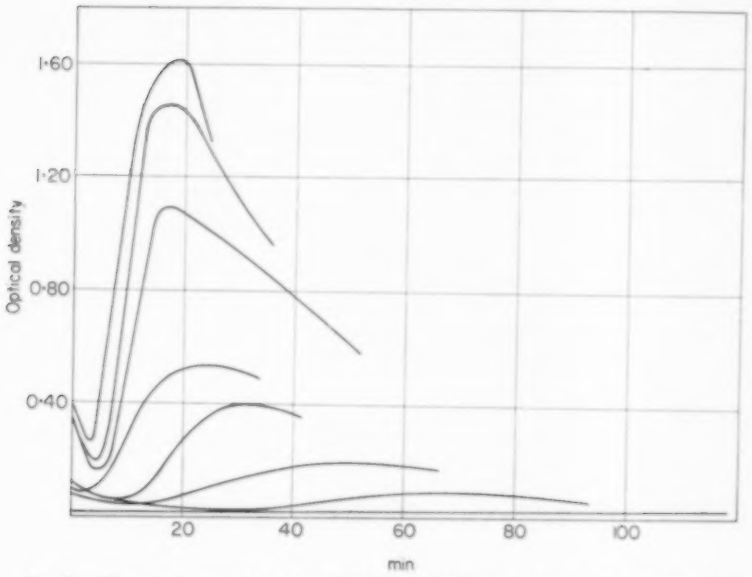



FIG. 5.—Change of optical density at 330 mμ with time for various dilutions of the stock solution of cobaltic perchlorate. Temperature = 28·00°C, $[HClO_4]$ = 0·339 M, cell length = 1 cm. The ends of the curves denote the times at which the chemical analyses were made.

TABLE 1

| Temp. = 32·00°C $[HClO_4]$ = 0·305 M | | | Temp. = 28·00°C $[HClO_4]$ = 0·339 M | | | Temp. = 20·00°C $[HClO_4]$ = 0·330 M | | |
|---|---|---|---|---|---|---|---|---|
| [Co(III)] (M) | $\varepsilon_{obs}$ | Time (min) | [Co(III)] (M) | $\varepsilon_{obs}$ | Time (min) | [Co(III)] (M) | $\varepsilon_{obs}$ | Time (min) |
| $10{\cdot}1 \times 10^{-3}$ | 102 | 14 | $15{\cdot}0 \times 10^{-3}$ | 87 | 21 | $18{\cdot}6 \times 10^{-3}$ | 62 | 58 |
| 8·4 | 82 | 18 | 11·6 | 82 | 36 | 12·2 | 43 | 78 |
| 8·2 | 94 | 18 | 8·9 | 55 | 33 | 9·2 | 33 | 127 |
| 6·8 | 63 | 20 | 8·7 | 69 | 52 | 8·6 | 41 | 240 |
| 5·0 | 60 | 40 | 7·6 | 48 | 41 | 6·0 | 26 | 175 |
| 4·0 | 43 | 38 | 5·2 | 34 | 66 | 2·5 | 11 | 250 |
| 2·5 | 32 | 47 | 3·4 | 26 | 85 | | | |
| 1·1 | 17 | 60 | 1·6 | 13 | 130 | | | |

that at 20°C a complex of high extinction coefficient is formed slowly and therefore cannot be a primary product of the electrolysis. Some solutions were prepared from the 20°C stock solution which only differed in the concentration of Co(III) ion and these were allowed to stand for at least 2 hr; their optical densities at 330 mμ were then measured, and they were analysed for Co(III). The results obtained (Table 2) are to be compared with those presented in Table 1 and Fig. 4 for a temperature of 20·00°C. The data in Table 2 do not show a simple relationship for the cobaltic ion concentration dependence, and hence it may be concluded that chemical equilibrium

is not attained even after an interval of 2 hr. However, the higher values of the extinction coefficient obtained suggest that the electrolytic process has been able to compete successfully with the reduction of Co(III) by water and thus enable a greater concentration of the complex to be formed.

## DISCUSSION

The main fact emerging from the above study is that high cobaltic perchlorate concentrations and low acidities favour at least one Co(III) species whose absorption

TABLE 2
$[HClO_4]$ = 0·315 M, temp. = 20·00°C, ionic strength = 1·1 to 1·3 M

| [Co(III)] (M) | $\varepsilon_{obs}$ at 330 mμ |
|---|---|
| $10{\cdot}4 \times 10^{-3}$ | 74 |
| 5·0 | 76 |
| 3·5 | 66 |
| 1·6 | 16 |

spectrum is markedly different from that which we assume to be $Co^{3+} \cdot 6H_2O$. The evidence obtained is consistent with the tentative mechansim:

$$Co^{3+} + H_2O \rightleftharpoons CoOH^{2+} + H^+ \qquad \text{(rapid)}$$

$$Co^{3+} + CoOH^{2+} \rightarrow Co{-}O{-}Co^{4+} + H^+$$
$$\text{and/or} \quad CoOH^{2+} + CoOH^{2+} \rightarrow Co{-}O{-}CoOH^{3+} + H^+ \qquad \text{(slow)}$$

There are of course possibilities that the dimer may hydrolyse further or form higher polynuclear species. The basic Co—O—Co dimer structure is favoured rather than the one postulated for the iron dimer,[2] i.e. $Fe(OH)_2Fe^{4+}$, because the large changes observed in the absorption spectrum might well be the result of forming relatively strong bonds. Further support for this idea comes from the virtual irreversibility of the dimerization reaction.

FRIEDMAN *et al.*[5] using a modified Quincke method, measured the magnetic susceptibility at 1°C of cobaltic perchlorate solutions having a perchloric acid concentration of 4 M and found them to be diamagnetic; presumably the Co(III) concentration was as high as could be obtained, i.e. about 0·1 M. From the data provided by the present study it may be concluded that these conditions would favour monomeric species of Co(III), in which case the ion $Co^{3+} \cdot 6H_2O$ must be diamagnetic. On the other hand, BAXENDALE and WELLS[4] concluded from their investigation of the kinetics of the reaction of Co(III) with water that the predominant entity is a dimer. This proposal agrees with our evaluation of the system, since the conditions which they employed would be expected to yield a high proportion of polymeric species. Positive identification of the species present in cobaltic perchlorate solutions, and the determination of their formation constants, must await a new experimental approach which can cope with the difficulty of handling the highly reactive Co(III) solutions.

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 287 to 296. Pergamon Press Ltd. Printed in Northern Ireland

# THE ANION EXCHANGE OF METAL COMPLEXES—IV
## THE IRON(III)–CHLORIDE SYSTEM*

Y. MARCUS
Israel Atomic Energy Commission Laboratories, Rehovoth

(*Received* 12 *September* 1958; *in revised form* 17 *December* 1958)

**Abstract**—The anion exchange method described in previous communications was applied to the iron(III)–chloride complex system. The distribution of iron was determined by the batch method. The mononuclearity of the complexes was confirmed for the range $10^{-3}$–$4 \times 10^{-2}$ M iron. Distribution curves were obtained for the range 1·0–12 M chloride in lithium chloride and hydrochloric acid solutions. Up to 9 M chloride there is no hydrogen-ion effect, but for more concentrated solutions of hydrochloric acid the distribution is lower than for lithium chloride solutions. Both curves show a maximum. A corrected distribution curve was constructed for the lithium chloride experiments, showing the complexes $FeCl_2^+$, $FeCl_2$ and $FeCl_4^-$, with the successive stepwise formation constants

$$\log k_2 \geq -0{\cdot}7, \quad \log k_3 = -1{\cdot}40 \quad \text{and} \quad \log k_4 = -1{\cdot}92.$$

In addition to these species, some undissociated $HFeCl_4$ is also formed in concentrated hydrochloric acid. Spectrophotometric measurements in concentrated chloride solutions confirm these results qualitatively.

Vol.
12
59/60

## INTRODUCTION

GAMLEN and JORDAN[1] have recently published a study of the iron(III)–chloride complex system in concentrated chloride solutions. The solvent extraction of iron from concentrated hydrochloric acid solutions has been investigated by numerous authors.[2] It appears from this that although the iron(III) cation is not very much complexed in dilute chloride solutions, it is strongly complexed in concentrated solutions. Many authors[3] have dealt with the first complex formed, $FeCl^{2+}$, and found its formation constant at different ionic strengths. Constants for higher complexes have not been so well reported (Table 6) and the authors do not agree very well. The anion exchange method[4] should be useful in deciding on the magnitude of the constants. In particular the constants for $FeCl_2$ and $FeCl_4^-$, species with zero or unit charge, can be obtained with little error, as has been shown.[4]

It is well known that iron is absorbed from concentrated hydrochloric acid on to anion exchangers. MOORE and KRAUS[5] in a short communication presented data

* This work is taken from part of a Ph.D. thesis submitted to the Hebrew University, Jersualem, 1955. A preliminary presentation of the contents was given at the 16th meeting of the Israel Chemical Society, Jerusalem, December 1954.

[1] G. A. GAMLEN and D. O. JORDAN, *J. Chem. Soc.* 1435 (1953).

[2a] N. H. NACHTRIEB and J. G. CONWAY, *J. Amer. Chem. Soc.* **70**, 3547 (1948); [2b] N. H. NACHTRIEB and R. E. FRYXELL, *Ibid.* **70**, 3552 (1948); [2c] R. C. MYERS, D. E. METZLER and E. H. SWIFT, *Ibid.* **72**, 3767 (1950); [2d] **72**, 3772 (1950); [2e] D. E. METZLER and R. C. MYERS, *Ibid.* **72**, 3776 (1950); [2f] N. H. NACHTRIEB and R. E. FRYXELL, *Ibid.* **74**, 897 (1952); [2g] D. E. CHALKLEY and R. J. P. WILLIAMS, *J. Chem. Soc.* 1920 (1955); [2h] J. AXELROD and E. H. SWIFT, *J. Amer. Chem. Soc.* **62**, 33 (1940).

[3a] W. C. BRAY and A. V. HERSHEY, *J. Amer. Chem. Soc.* **56**, 1889 (1934); [3b] M. MOLLER, *J. Phys. Chem.* **41**, 1123 (1937); [3c] C. BROSSET, *Naturwissenshaften* **29**, 455 (1941); [3d] J. BADOZ-LAMBLING, *Bull. Soc. Chim. Fr.* 552 (1950).

[4] Part I: Y. MARCUS and C. D. CORYELL, *Bull. Res. Council Israel* **8A**, 1 (1959).

[5] G. E. MOORE and K. A. KRAUS, *J. Amer. Chem. Soc.* **72**, 5792 (1950).

for the distribution of iron between Dowex-1 resin and hydrochloric acid at eight concentrations between 0·5 and 9·0 M. Many authors have since made use of the absorption of iron (and its desorption at lower chloride concentrations) in their investigations. Some additional data have been published on the absorption of iron under specific conditions, but no detailed study of its distribution between lithium chloride and hydrochloric acid solutions and a strongly basic anion exchanger like Dowex-1 could be found. The present study undertakes such an investigation in concentrated chloride solutions, 1–12 M as function of three variables, the concentrations of iron(III), chloride and hydrogen ions.

## EXPERIMENTAL

All reagents used were of analytical grade, except the resin, which was purified by usual methods, and the lithium chloride, which was purified as described before.[6] Iron solutions were prepared by diluting a stock solution, made by dissolving iron(III) chloride hexahydrate in diluted (1 : 1) hydrochloric acid. In order to repress hydrolysis, acid was added to the iron and lithium chloride solutions to give a final concentration of around 0·06 M. Iron was assayed colorimetrically by the thiocyanate–acetone method.[7] This fixed the lower level of measurable concentrations at $2 \times 10^{-5}$ M. Chloride was determined as described before.[6]

The resin was chloride, 10 per cent crosslinked Dowex-1 with a capacity of 2·3 m equiv. g, and was used in two forms. One was air-dried resin with water content of 44 per cent and 20 to 50 mesh size. The other was oven-dried at 110°C, containing only 1–3 per cent water and ground to 100–200 mesh size. Results were calculated on the basis of the air-dried resin for comparison with the other systems studied, the agreement between the results with the two kinds of resin being within ±4 per cent.

In early experiments, chlorine water was added to the solutions to counteract an assumed reduction of iron by the resin. It was observed, however, that no reduction occurs, and the same results were obtained with and without chlorine, and its use was therefore subsequently discontinued.

The resin was shaken with the solution for 16–20 hr at 25 ± 2 C. Ratios of solution volume to resin weight and initial iron concentrations were selected, where possible, so as to have of the order of one half of the iron in the resin.

For spectrophotometric measurements a Beckman DU quartz spectrophotometer was used. The light source was a tungsten lamp. The Corex cells used had light-paths of 1·000 ± 0·003 cm. The reference cell contained distilled water, since chloride ions do not absorb light at the wavelength employed, 500 mμ.

## RESULTS

The results of the anion exchange measurements are given in terms of $D$, the distribution coefficient, which is the ratio of the concentration of iron in moles per kg of air-dried resin to the molar concentration in solution at equilibrium. The concentration in the resin was obtained by difference. The expected errors in the distribution coefficients are within 5 per cent or 0·02 log units for most cases.

The initial concentration of iron was varied in one series of experiments in the range $1 \times 10^{-3}$ to $4 \times 10^{-2}$ M, with results as appearing in Table 1. It is seen that the distribution of iron remains, within limits of error, independent of the iron concentration. As loading was rather high in all cases, deviation could have occurred from this behaviour; in fact, only in the case of 0·0376 M iron solutions did the loading exceed 10 per cent, and the distribution coefficient was significantly lowered.

The results of varying the lithium chloride or the hydrochrolic acid concentrations appear in Tables 2 and 3. In many cases the data are the average of two or more

[6] Part III: Y. MARCUS, *J. Phys. Chem.* **63**, 1000 (1959).
[7] E. B. SANDELL, *Colorimetric Determination of Traces of Metals* (2nd Ed.) p. 373 Interscience, New York (1950).

Vol. 12 1959/6

TABLE 1.—EFFECT OF THE VARIATION OF THE IRON CONCENTRATION

| Chloride concentration (M) | Hydrogen ion concentration (M) | Initial iron concentration (mM) | Equilibrium iron concentration (mM) | Log of iron distribution coefficient log $D$, l. kg$^{-1}$ |
|---|---|---|---|---|
| 3·8 | 3·8 | 1·1 | 0·34 | 2·39 |
| | | 2·7 | 0·63 | 2·43 |
| | | 5·0 | 0·83 | 2·36 |
| | | 9·9 | 0·92 | 2·40 |
| 7·7 | 0·03 | 1·9 | 0·012 | 3·81 |
| | | 3·6 | 0·021 | 3·78 |
| | | 9·7 | 0·032 | 3·80 |
| | | 20·6 | 0·040 | 3·78 |
| | | 37·6 | 0·082 | 3·71 |

TABLE 2.—EFFECTS OF THE VARIATION OF THE LITHIUM CHLORIDE CONCENTRATION

| LiCl conc. ($M_{Cl}$) | Log of Cl activity function log $a$ | Log of iron distribution coefficient log $D$ | LiCl conc. ($M_{Cl}$) | Log of Cl activity function log $a$ | Log of iron distribution coefficient log $D$ |
|---|---|---|---|---|---|
| 1·7 | 0·20 | 0·80 ± 0·2 | 7·8 | 1·90 | 3·78 |
| 3·0 | 0·68 | 1·68 | 8·3 | 2·00 | 3·82 |
| 3·3 | 0·78 | 1·83 | 8·7 | 2·13 | 3·82 |
| 5·0 | 1·20 | 2·75 | 9·9 | 2·40 | 3·86 |
| 6·0 | 1·42 | 3·25 | 10·9 | 2·60 | 3·87 |
| 6·6 | 1·60 | 3·43 | 11·7 | 2·78 | 3·79 |
| 6·8 | 1·65 | 3·48 | 11·9 | 2·80 | 3·78 |

determinations with similar results. The ligand activity function $a$ represents $M_{LiCl}\gamma_{\pm(LiCl)}$ or $M_{HCl}\gamma_{\pm(HCl)}$ as the case may be. The data recorded in Tables 2 and 3 are shown in Fig. 1 as curves of log $D$ vs. log $a$.

The effect of varying the hydrogen ion concentration at constant chloride concentration is shown in Table 4. The values in italics are interpolated from Fig. 1.

Results of spectrophotometric measurements, made at a wavelength of 500 m$\mu$ (the absorption band of iron(III) chloride ranges from about 380 to about 540 m$\mu$), are reported in Table 5.

## DISCUSSION

Tables 1 and 5 show two properties of the iron which are independent of its concentration in the range 1–40 mM, viz. the anion exchange distribution and the molar extinction. It is thus most likely that the complex species existing in the solutions are mononuclear. Other authors have found similar behaviour for light absorption[2a, f] and also for solvent extraction.[2a–g] Although disagreement prevails about polymerization in the organic solvent, it is agreed that polymerization does not occur in the aqueous phase.

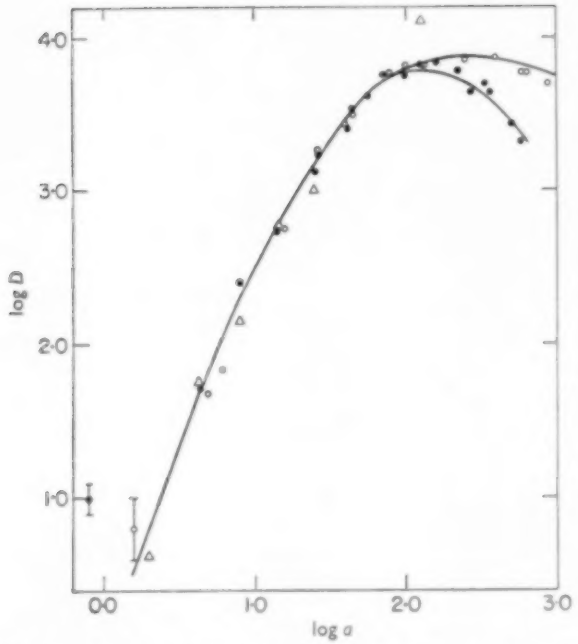



FIG. 1.—The anion exchange distribution of iron(III) between the resin Dowex-1 and hydrochloric acid or lithium chloride solutions; the logarithm of the distribution coefficient, log $D$, plotted vs. the logarithm of the chloride activity function log $a$. ○ lithium chloride solutions, ● hydrochloric acid solutions, △ data from (5) for hydrochloric acid, solid lines: calculated by equation (9).

Vol. 12 1959/6

TABLE 3.—EFFECT OF THE VARIATION OF THE HYDROCHLORIC ACID CONCENTRATION

| HCl conc. ($M_{HCl}$) | Log of Cl activity function log $a$ | Log of iron distribution coefficient log $D$ | HCl conc. ($M_{HCl}$) | Log of Cl activity function log $a$ | Log of iron distribution coefficient log $D$ |
|---|---|---|---|---|---|
| 1·0 | −0·10 | 1·0 ± 0·1 | 8·3 | 2·00 | 3·76 |
| 2·9 | 0·63 | 1·71 | 8·7 | 2·13 | 3·82 |
| 3·8 | 0·90 | 2·40 | 9·1 | 2·20 | 3·83 |
| 4·9 | 1·15 | 2·74 | 9·7 | 2·35 | 3·78 |
| 5·7 | 1·40 | 3·13 | 10·0 | 2·43 | 3·65 |
| 5·9 | 1·42 | 3·23 | 10·3 | 2·52 | 3·70 |
| 6·6 | 1·62 | 3·40 | 10·8 | 2·56 | 3·65 |
| 6·8 | 1·64 | 3·54 | 11·4 | 2·70 | 3·41 |
| 7·3 | 1·75 | 3·61 | 11·6 | 2·75 | 3·32 |
| 7·7 | 1·85 | 3·77 | | | |

Table 2 and Fig. 1 (the lithium chloride curve) show the effect of varying the chloride concentration on the anion exchange distribution of iron. The hydrogen ions present (no more than 0·1 M) are not expected to have any effect besides repressing hydrolysis. It may be calculated from the constants given by RABINOWITCH and

TABLE 4.—EFFECT OF THE VARIATION OF THE HYDROGEN ION CONCENTRATION AT CONSTANT CHLORIDE ION CONCENTRATION

| Chloride concentration (M) | Hydrogen ion concentration (M) | Log of iron distribution coefficient, log $D$ l./kg | |
|---|---|---|---|
| | | observed | calc. equation (12) |
| 2·9 | *0·03* | 1·65 | |
| | 1·0 | 1·59 | |
| | 2·9 | 1·71 | |
| 5·7 | *0·06* | 3·11 | |
| | 1·9 | 3·11 | |
| | 3·8 | 3·15 | |
| | 5·7 | 3·13 | |
| 8·7 | *0·08* | 3·82 | |
| | 2·9 | 3·77 | |
| | 5·7 | 3·85 | |
| | 8·7 | 3·82 | |
| 9·7 | *0·06* | 3·86 | 3·87 |
| | 3·2 | 3·83 | 3·85 |
| | 6·4 | 3·81 | 3·80 |
| | 9·7 | 3·78 | 3·77 |
| 10·3 | *0·06* | 3·84 | 3·88 |
| | 3·6 | 3·83 | 3·82 |
| | 6·7 | 3·79 | 3·75 |
| | 10·3 | 3·70 | 3·69 |
| 11·4 | *0·06* | 3·78 | 3·74 |
| | 3·7 | 3·65 | 3·64 |
| | 7·6 | 3·57 | 3·56 |
| | 11·4 | 3·42 | 3·42 |

STOCKMAYER[8] that under the worst circumstances, the relative concentration of hydrolysed species, as $FeOH^{2+}$, is 3 per cent.

In order to interpret the data, the mathematical relationship between the distribution coefficient $D$ and the chloride activity function $a$ must be found. A detailed derivation of such an expression has been reported,[4] and here only the main points and equations will be given.

[8] E. RABINOWITCH and W. C. STOCKMAYER, *J. Amer. Chem. Soc.* **64**, 335 (1942).

The complex species of iron may be considered to be formed in a reaction

$$FeCl_3 \rightleftharpoons FeCl'^{i}_{3-i} + iCl^- \quad (1)$$

where $i$ is the charge of the complex. The concentration of the iron species will be given by

$$\Sigma M_i' = a_0'\Sigma\beta_i'^{*}a^{-i} \quad (2)$$

where $a'_0$ is the thermodynamic activity of the neutral species $FeCl_3$, and $\beta'_i{}^*$ are

TABLE 5.—LIGHT ABSORPTION OF IRON IN CHLORIDE SOLUTIONS AT 500 mμ

| Chloride conc. (M) | Hydrogen ion conc. (M) | Iron conc. (mM) | Molar extinction ($M^{-1}$ $cm^{-1}$) |
|---|---|---|---|
| 3·0 | 0·04 | 10 | 5·0 |
| | 0·04 | 42 | 5·0 |
| | 3·0 | 9 | 5·0 |
| | 3·0 | 39 | 5·0 |
| 7·0 | 0·10 | 4 | 26 |
| | 0·10 | 64 | 25 |
| | 2·3 | 4 | 26 |
| | 4·7 | 4 | 27 |
| | 7·0 | 4 | 26 |
| 9·8 | 0·08 | 9 | 48 |
| | 0·08 | 41 | 50 |
| | 9·8 | 8 | 36 |
| | 9·8 | 41 | 38 |
| 11·9 | 0·03 | 9 | 70 |
| | 4·0 | 12 | 45 |
| | 7·9 | 9 | 35 |
| | 11·9 | 9 | 20 |

complexity parameters involving the thermodynamic equilibrium constants and activity coefficient functions, which are assumed constant (see discussion in Part I[4]).

Much evidence has been presented to the effect that the limiting complex in aqueous solutions is $FeCl_4^-$.[1,9] The resin complex would then be $RFeCl_4$, and the charge number in the resin (called $-p$ in)[4] will have the value $i = -p = -1$. The concentration of iron in the resin is then given by an expression analogous to equation (2)

$$_rM_{FeCl_4^-} = {}_rM'_{-p} = {}_ra_0'\,{}_r\beta'^{*}_{-p}\,{}_ra^p \quad (3)$$

With the same standard states in both phases, it is easy to see that ${}_ra'_0 = a'_0$, and thus the distribution coefficient, which is the ratio of the quantities given in equations (3) and (2) will be given in the logarithmic form as

$$\log D = \log ({}_rM'_{-p}/\Sigma M'_i) = \log {}_r\beta'^{*}_{-1} + \log {}_ra - \log \Sigma\beta'^{*}_i a^{-i} \quad (4)$$

[9] H. L. FRIEDMAN, *J. Amer. Chem. Soc.* **74**, 5 (1952).

Vol. 12 1959/6

Now ${}_{r}a = {}_{r}M_{LiCl}\,{}_{r}\gamma'_{LiCl}$ may be related to $a$ by ([4] equation 26)

$$\log {}_{r}a = \log a + \tfrac{1}{2}(\log {}_{r}M_{Cl} - \log {}_{r}M_{Li}) \tag{5}$$

and is a measurable quantity. Calling its value ${}_{r}a^{0}$ at $a = 1$, a correction function ${}_{r}F_{a}$ is defined as

$$ {}_{r}F_{a} = \log {}_{r}a - \log {}_{r}a^{0} \tag{6}$$

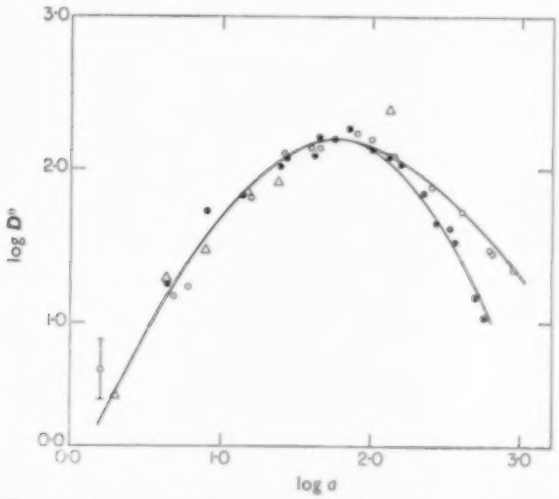



FIG. 2.—The corrected distribution curves for the anion exchange of iron(III); the logarithm of the corrected distribution coefficient, log $D^{0}$, equation (9), plotted vs. the logarithm of the chloride activity function log $a$. The experimental points were obtained from values in Fig. 1 by log $D^{0} = \log D - {}_{r}F_{a}$. The same symbols as in Fig. 1 are used.

Finally, if we define $K_{r}' = {}_{r}\beta'^{*}_{-1}\,{}_{r}a^{0}$, and a corrected or ideal distribution coefficient $D^{0}$ by $\log D^{0} = \log D - p_{r}F_{a}$, the expression

$$\log D^{0} = \log K_{r}' - \log \Sigma \beta_{i}'^{*} a^{-i} \tag{7}$$

is obtained.

Values of ${}_{r}F_{a}$, the correction function, were obtained from Fig. 1 of reference (4), and a curve of log $D^{0}$ vs. log $a$ is plotted in Fig. 2. The curve has slopes ranging from approximately $+1{\cdot}5$ at the lowest chloride concentrations to $-1{\cdot}00$ at 9–12 M lithium chloride. The slopes are directly connected with the charge numbers $\bar{\imath}$ (analogous to the ligand numbers of BJERRUM $\bar{n}$, here $\bar{n} = 3 - \bar{\imath}$):

$$\frac{d(\log D^{0})}{d(\log a)} = \bar{\imath} \tag{8}$$

since the parameters $K_{r}'$ and $\beta_{i}'^{*}$ are taken as constants. The charge numbers of the complexes $FeCl_{3-i}^{i}$ are seen to range from $i = 2$ for $FeCl^{2+}$ to $i = -1$ for $FeCl_{4}^{-}$.† The "half-integral $\bar{\imath}$" method[10] was used to obtain preliminary values of the constants $k_{i}'^{*} = \beta_{i}'^{*}/\beta_{i-1}'^{*}$. For the constant $k_{2}'^{*}$ only an upper limit could be obtained, since

† A single experimental point at 12·7 M lithium chloride with log $D = 3{\cdot}71$ seems to indicate a slope more negative than $-1{\cdot}00$, using a value of ${}_{r}F_{a}$ extrapolated from experimental data below 12 M lithium chloride. Since this extrapolation is uncertain, it is not profitable to interpret this particular experimental datum.

the data are not accurate at low chloride concentrations. It was used in a correction term permitting the evaluation of $k'_1{}^*$ and $k'^*_{-1}$ for the formation of $FeCl_2^+$ and $FeCl_4^-$ from $FeCl_3$, by the "curve fitting" method.[10] The final constants obtained are:

$$\log k_2'^* \leq 0{\cdot}7 \qquad \log k_1'^* = 1{\cdot}40 \pm 0{\cdot}06 \qquad \log k'^*_{-1} = -1{\cdot}92 \pm 0{\cdot}08$$

$$\log K_r' = 2{\cdot}41 \pm 0{\cdot}03$$

Curves calculated with these parameters for $\log D^0$ and $\log D$ (equation (9)) are shown in Figs. 1 and 2 to agree well with the data.

$$\log D = \log D^0 + {}_rF_a = \log K_r' + {}_rF_a - \log (k_2'^* k_1'^* a^{-2} + k_1'^* a^{-1} + 1 + k'^*_{-1} a) \tag{9}$$

The parameter $K_r'$ is transformed to the equilibrium constant for the formal resin absorption reaction

$$FeCl_3\,(aq) + RCl \rightleftharpoons RFeCl_4 \tag{10}$$

by dividing it by the resin reference activity function ${}_ra^0$, obtained from reference (10): $\log K_r' - \log {}_ra^0 = 2{\cdot}41 - 0{\cdot}46 = 1{\cdot}95$. This value may be compared with the corresponding parameter for the solution phase, $\log k'^*_{-1} = -1{\cdot}92$. The stabilization factor for the resin complex is seen to have the large value of about 7000.

*The hydrogen ion effect*

Tables 3, 4 and 5 show the effects of varying the hydrogen ion concentration. Consideration of these tables shows that up to 9 M chloride there is no appreciable difference of behaviour between lithium chloride and hydrochloric acid solutions, i.e. the same anion exchange distribution coefficient $D$ and the same molar extinction are obtained for a given value of the chloride activity function $a$. Above 9 M chloride, increase of hydrogen ion concentration at fixed chloride concentrations decreases both the distribution coefficient and the molar extinction to an amount not explicable by differences in $a$.[11]

The question whether differences in distribution coefficients for lithium chloride and hydrochloric acid solutions are, in the general case, due to the formation of a new species, a chloro-acid, is controversial.[6] Changes in light absorption are, however, more difficult to attribute to another cause. The data can be interpreted as the formation of a species with relative concentration dependent on the hydrochloric acid activity at a given chloride concentration having a lower molar extinction and which is not absorbed by the resin. As these effects are shown only above 9 M chloride, where $FeCl_4^-$ becomes more important than $FeCl_3$, this species is probably the undissociated $HFeCl_4$.

The species $HFeCl_4$ has been identified by many authors in organic solvents,[2a,d,h] although FRIEDMAN[9] considers it rather to be an ion-pair $H_3O^+$-$FeCl_4^-$. As regards aqueous, concentrated hydrochloric acid he thinks these ions are separated (ionization of $HFeCl_4$ is as complete as that of HCl). Since the activity of hydrochloric acid

[10] Part II: Y. MARCUS, *Bull. Res. Council Israel* **8A**, 17 1959).

[11] For the so-called "lithium chloride effect" see e.g. Y. MARCUS, *Bull. Research Council, Israel* **4**, 326 (1954); K. A. KRAUS, F. NELSON, F. B. CLOUGH and R. C. CARLSTON, *J. Amer. Chem. Soc.* **77**, 1391 (1955).

increases fortyfold between 5 and 12 M, the observation of no difference in the extraction of iron from 5 M sodium chloride and 5 M hydrochloric acid, does not imply, as METZLER and MYERS[2e] propose, that $HFeCl_4$ is necessarily completely dissociated in concentrated hydrochloric acid.

A quantitative measure of the proton association with $FeCl_4^-$ may be obtained from the anion exchange distribution measurements. For the reaction $FeCl_3 + H^+ + Cl^- \rightleftharpoons HFeCl_4$, the equilibrium constant is

$$ {}_1\beta'^{*}_{-1} = M_{HFeCl_4}/M_{FeCl_3}a^{-2} \qquad (11) $$

if one assumes the ratio of the activity coefficients of the uncharged species $FeCl_3$ and $HFeCl_4$ to be unity. The slope of the hydrochloric acid branch of the log $D^0$ curve

TABLE 6.—COMPARISON OF COMPLEX FORMATION CONSTANTS FOR THE IRON(III) CHLORIDE SYSTEM[12]

| Author | Method | Temp. (°C) | Medium | $\log k'_1{}^* = -\log k_3{}^*$ | $\log k'^*_{-1} = \log k_4{}^*$ |
|---|---|---|---|---|---|
| RABINOWITCH and STOCKMAYER[5] | sp | 26·7<br>25 | I(H, $NaClO_4$)<br>→0 | 1·40<br>1·0 | |
| OLERUP[13] | sp, red | 20 | 2($HClO_4$) | 0·06 | |
| GAMLEN and JORDAN[1] | sp | 20 | 0 corr | 0·14 | −1·98 |
| This work | an ex | 25 | 0 corr | 1·40 | −1·92 |

in Fig. 2 yields the value $\log {}_1\beta'^{*}_{-1} = -4{\cdot}6 \pm 0{\cdot}1$. The acid $HFeCl_4$ is thus formed only in very concentrated hydrochloric acid, at values of $\log a \geq 2{\cdot}3$. Curves of log $D^0$ and log $D$ were calculated using a modification of equation (9) by adding ${}_1\beta^{*}_{-1}a^{-2}$ to the term in brackets, and are shown in Figs. 1 and 2 to fit the data well.

It is very difficult to interpret the data obtained for mixtures of lithium chloride and hydrochloric acid solutions. (The small amount of hydrochloric acid in the lithium chloride solutions discussed in the previous section is negligible). Activity coefficients are not known for these mixtures, as also the proper mixed resin activity function ${}_rF_a$. Making the very rough approximations of using $\gamma_{\pm HCl}$ and the ${}_rF_a$ values for hydrochloric acid as applying also to the mixtures, equation (12) was used for computing the values in the last column of Table 4:

$$ \log D = \log K_r' - \log (1 + k'^{*}_{-1}M_{Cl}\gamma_{\pm HCl} + {}_1\beta'^{*}_{-1}M_{Cl}M_H\gamma^2_{\pm HCl}) + {}_rF_a \qquad (12) $$

These values are seen to agree reasonably well with the experimental values.

The distribution data for hydrochloric acid solutions may be compared with those of MOORE and KRAUS,[5] who worked with the same resin, Dowex-1. In order to convert their volume distribution coefficients to the weight distribution coefficients used here, it is necessary to multiply them by the factor 2·2, the specific volume of the wet resin. The values appearing in Fig. 1 are then obtained, which are seen to be

[12] J. BJERRUM, G. SCHWARZENBACH and L. G. SILLEN (Compilors), *Stability Constants of Metal-ion Complexes. Part II: Inorganic Ligands* p. 97. Special publication No. 7 of the Chemical Society, London (1958). This reference defines the terms entered under "Method" and "Medium".

[13] H. OLERUP, *Svensk kem. Tidskr.* **55**, 324 (1943).

in good agreement with those obtained in this work, except for the high value at 9 M hydrochloric acid. Their value for 2 M acid should be more reliable than the one obtained here, since the column method is superior at low $D$ values, and it was used to fix the lower part of the curve in Fig. 1.

The complex formation parameters obtained may be compared with those reported in the literature, Table 6.

The value of $k'^{*}_{-1}$ found here agrees well with the value of $k_4^*$ given by GAMLEN and JORDAN, but the value of $k'_1{}^*$ is more in line with $k_3$ of RABINOWITCH and STOCKMAYER, although different media are involved with the latter. A discussion of the relationship between starred parameters (i.e. those reported in this work and in that of GAMLEN and JORDAN) and complexity constants valid for infinite dilution or constant ionic strength must be deferred (see references (1), (4), (10)). The data available do not cover a range that will make possible the evaluation of $k'_2{}^*$ or $k_2^*$ for the formation of $FeCl_2^+$ from $FeCl_3$ or from $FeCl^{2+}$.

*Acknowledgement*—Thanks are due to the Director of Research, Israel Atomic Energy Commission, for his help and encouragement.

Vol
12
1959/

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 297 to 303. Pergamon Press Ltd. Printed in Northern Ireland

# DOSAGE RADIOCHIMIQUE DU CÉSIUM PAR COLORIMÉTRIE DE LA DIPICRYLAMINE

A. M. LEFEVRE, J. F. LEFEVRE et A. RAGGENBASS
Dept. de Chimie, Centre d'Etudes Nucléaires de Saclay, Saclay

(*Received* 1 *May* 1959)

**Résumé**—Le césium est précipité sous forme de dipicrylaminate qui, après lavage à l'éther, est dissout dans l'acétate d'éthyle; le césium est extrait de cette solution par une solution aqueuse acide. La phase acétate d'éthyle, contenant la dipicrylamine provenant de la décomposition du dipicrylaminate de césium est alors dosée colorimétriquement. L'intérêt principal de cette méthode consiste en la possibilité d'affectuer le dosage radiochimique du césium (avec entraîneur) en décontaminant la solution introduite dans le spectrophotomètre.

L'EMPLOI en analyse de la dipicrylamine (22′, 44′, 66′ hexanitrodiphénylamine) a été étudié par de nombreux auteurs, principalement pour le dosage du potassium. Depuis SHEINTZIS[1] qui, le premier, étudia en détail les applications analytiques de ce réactif, les méthodes les plus variées ont été décrites:* gravimetrié, conductimétrie, ampérométrie, potentiométrie, polarographie, colorimétrie directe ou indirecte.[2–10]

En utilisant les différences de solubilité des dipicrylaminates dans les solvants organiques ou mélanges de solvants, il a été réalisé certains dosages colorimétriques[5,10] et même des séparations des métaux alcalins.[6]

Le réactif de précipitation est le sel de magnésium ou de lithium, quelquefois de magnésium sodium ou de calcium.

Des méthodes de dosages quantitatifs du césium ont été décrites[1,4,6,9,11–13] nous nous sommes surtout intéressés aux travaux de HAHN et BAKER,[9] et KOURIM et KRTIL[13] traitant du dosage de césium dans les produits de fission, ce qui était également le but de notre travail.

## I. PRINCIPE DU DOSAGE

Les différentes méthodes colorimétriques déjà décrites utilisent soit, directement, la coloration dûe au précipité redissout dans un solvant, soit, indirectement, la mesure colorimétrique de l'excès

* La bibliographie complète, trop importante, n'a pas été reproduite ici, seules les principales références concernant la colorimétrie et le dosage du césium ont été conservées.

[1] O. G. SHEINTZIS, *Zavodskaya Lab.* **4**, 1047 (1935); **8**, 1198 (1939); **9**, 162–3 (1940); *J. Appl. Chem. U.S.S.R.* **11**, 1012 (1938); **13**, 1098 (1940); *Chem. Zentr* **1**, 2434–5 (1942); O. G. SHEINTZIS et M. V. GAPCHENKO, *Zavodskaya Lab.* **14**, 440 (1948).
[2] K. LAWTON, *Soil. Sci. Soc. Amer. Proc.* **10**, 126 (1946).
[3] W. KÖHN, *Z. Anal. Chem.* **128**, 1–6 (1947).
[4] W. D. TREADWELL et H. HEPENSTRICK, *Helv. Chim. Acta* **32**, 1903–10 (1949).
[5] R. BELMAS, *Rev. Géné. Caoutchouc* **26**, 341 (1949).
[6] S. SHOZO, *Bunseki to Shiyaku* **3**, 55–64 (1949); *J. Chem. Soc. Japan* **72**, 182, 249, 420, 593, (1951).
[7] S. SHOZO et U. ZEN-ICHI, *J. Chem. Soc. Japan* **73**, 2, 4 (1952).
[8] P. R. LEWIS, *Analyst* **80**, 955, 768–780 (1955).
[9] R. B. HAHN et R. O. BAKER, AECU–2903 (1955); *Nucleonics* **14**, 90–95 (1956).
[10] S. KERTES et J. M. E. GOLDSCHMIDT, *J. Chem. Soc.* 401–4 (1956).
[11] N. et T. YAMAGATA et S. WATANABE, *Bull. Chem. Soc. Japan* **30**, 577–80 (1957).
[12] I. M. KORENMAN et G. A. SHATALINA, *J. Anal. Khim.* (*U.S.S.R.*) **13**, 299–303 (1958).
[13] V. KOURIM et J. KRTIL, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, A/Conf/15/P2098.



Vol. 12 59/60

de réactif. Dans le cas de dosages sur des solutions radioactives, la mesure au colorimètre, d'après les méthodes précédentes, s'effectuerait alors sur des solutions radioactives. La méthode de dosage que nous proposons permet d'éviter cet inconvénient en décontaminant la solution servant à la mesure colorimétrique.

Le césium est précipité quantitativement[12] sous forme de dipicrylaminate en utilisant comme réactif un excès d'une solution de dipicrylaminate de magnésium à 3 pour cent. Le précipité obtenu est lavé soigneusement à l'éther éthylique afin d'éliminer l'excès de réactif (éventuellement extraction du sel d'ammonium[12]). Le précipité, après lavage, est dissout dans l'acétate d'éthyle et le césium extrait de cette solution par agitation avec une solution aqueuse chlorhydrique. La phase aqueuse séparée permet le comptage du césium, et la phase organique, décontaminée, le dosage colorimétrique de la dipicrylamine.

## II. REACTIFS—APPAREIL

*Nitrate de césium* "pur" (Prolabo).

*Dipicrylaminate de magnésium*, préparé à partir de la dipicrylamine (2,2′, 4,4′, 6,6′ hexanitrodiphénylamine)—"produit pour analyse" (Prolabo) suivant le procédé classique: 1·2 g de dipicrylamine est dissout avec 0·5 g de MgO dans 50 ml d'eau distillée. Agitation d'une heure. Repos durant 24 heures. Centrifugation et décantation ou filtration.

*Acétate d'éthyle*, "pour usage scientifique" (Prolabo).

*Le césium* a été marqué avec du $^{137}Cs$ sans entraîneur.

*Spectrophotomètre* D.K-2 (Beckman). Source utilisée: lampe à hydrogène. Cellules en silice.

## III. PRECIPITATION DU DIPICRYLAMINATE DE CESIUM

### (a) *Sélectivité*

La dipicrylamine (que nous symboliserons par DPA) n'est pas un réactif sélectif des alcalins lourds et il est indispensable d'effecteur une séparation préalable des ions gênants. Dans le cas des solutions de produits de fission, qui nous intéresse, une séparation préalable des autres radioéléments et impuretés peut être effectuée par précipitation sous forme d'hydroxydes ou de carbonates ou par toute autre méthode, échange d'ions par exemple.

Les essais de précipitation directe effectués par HAHN et BACKER[9] n'ont pas donné de bons résultats et, de même que KOURIM et KRTIL[13] ont adopté une élimination des impuretés par précipitation sous forme de carbonates avec utilisation de fer et strontium entraîneurs.

### (b) *Précipitation du césium*

Le mode opératoire de précipitation proposé par KOURIM et KRTIL[13] donne un rendement de 100 pour cent; il est le suivant: une prise d'essai de la solution à doser est chauffée à 60°–70°, un excès de 100 pour cent du réactif précipitant (solution à 3 pour cent de dipicrylaminate de magnésium) est ajouté avec une agitation continue. Le mélange est ensuite refroidi pendant 3 à 5 heures à 0–1°C et filtré sur verre fritté No 4 ou centrifugé. Le précipité est ensuite lavé en plusieurs fois par de l'éther éthylique anhydre.

Nous devons préciser qu'il est important de contrôler le pH de la solution à doser si l'on veut éviter une précipitation de la dipicrylamine (sous sa forme acide ou basique). Pour 20 ml d'une solution à laquelle on ajoute 8 ml de réactif, la zone de pH déterminée est 5–10·5. Le pH de précipitation, par effet tampon, se trouvant toujours être de 9·5. Les solutions à doser seront donc neutralisées jusqu'à virage du bleu de thymol (jaune–bleu pour pH 8·0–9·6).

Les solutions dosées contenaient 0·2 mg/ml de césium sous forme nitrate.

Vol. 12 1959/6

(c) *Lavages du précipité*

Le lavage à l'eau entraînant des pertes de précipité, il a été préféré plusieurs lavages à l'éther anhydre permettant une élimination complète de l'excès de réactif pouvant rester sur le précipité.

Dans le cas où les solutions contiendraient des traces d'ammonium, le dipicrylaminate d'ammonium serait éliminé à ce stade de la manipulation.

Si au contraire la quantité d'ammonium était plus importante, il serait nécessaire de traiter le mélange des dipicrylaminates suivant le procédé d'extraction à l'éther décrit par KOURIM et KRTIL.[13]

## IV. DISSOLUTION DU DIPICRYLAMINATE DE CESIUM DANS L'ACETATE D'ETHYLE ET EXTRACTION DU CESIUM PAR UNE SOLUTION CHLORHYDRIQUE

Nous avons remarqué que le dipicrylaminate de césium (que nous symboliserons par DPCs) était soluble dans l'acétate d'éthyle et qu'il était possible d'extraire quantitativement le césium en lavant la phase organique par une solution chlorhydrique. La phase acétate d'éthyle après extraction du césium contient la DPA qu'il est possible de doser colorimétriquement.

(1) *Dissolution du précipité.* La mise en solution à la température ambiante du DPCs dans l'acétate d'éthyle est rapide à partir de 4 mg de précipité par ml de solvant. Nous avons choisi arbitrairement de dissoudre 8·6 mg de DPCs (correspondant à un essai de 2 mg de césium) dans 10 ml d'acétate d'éthyle. La solution ainsi obtenue est limpide et rouge.

(2) *Extraction du césium.* En agitant la solution précédente avec une solution aqueuse chlorhydrique, il y a décomposition du sel de césium, ce dernier passant dans la phase aqueuse et le radical DPA restant dans la phase organique. Ceci se manifeste par le passage du rouge au jaune orangé de la phase acétate d'éthyle.

(A) *Influence de l'acidité de la solution chlorhydrique*

(a) *Sur la décontamination.* La décomposition du sel en présence d'eau a lieu très facilement, et, si l'on admet qu'un atome d'hydrogène remplace un atome de césium extrait, la quantité théorique serait sensiblement de 2 ml d'acide chlorhydrique N/100 pour 2 mg de césium.

En utilisant un excès de 100 pour cent d'acide chlorhydrique (2 ml de N/50) la décontamination a été totale après une agitation d'environ 3 min.

Les essais de décontamination ont été faits dans les conditions suivantes:

Pour un essai: 2 mg de césium, soit 8·6 mg de DPCs dans 10 ml d'acétate d'éthyle.
Activité mesurée: 50,000 coups/min par 10 ml.

Le compteur utilisé était un scintillateur $\gamma$ avec cristal creux permettant de mesurer, dans les conditions opératoires ci-dessus, un facteur de décontamination de 1000.

Les résultats sont donnés dans le Tableau 1.

*A fortiori* pour des solutions chlorhydriques plus concentrées la décontamination est meilleure et plus rapide.

(b) *Sur les conditions d'extraction et la colorimétrie.* Il a été effectué une série d'essais avec des solutions chlorhydriques de normalités N/100 jusqu'à N. Tous les essais correspondaient à 2 mg de césium dans 10 ml d'acétate d'ethyle (soit 8·6 mg de

DPCs ou 6·6 mg de DPA) extrait par 10 ml de solution aqueuse chlorhydrique. Les résultats sont donnés dans le Tableau 2.

En conclusion, les conditions d'extraction sont d'autant meilleures que les acidités sont plus fortes; cependant, le choix doit tenir compte de la stabilité de la coloration de la phase organique. Or, on peut observer une décoloration de la phase organique d'autant plus rapide qu'elle a été extraite par une solution plus acide. Ce phénomène est lent et une solution traitée par l'acide chloryhdrique N a une coloration stable durant au moins 48 hr.

Tableau 1

| Solution acétate d'éthy. | Solution d'extraction | Activité retrouvée ds.l'acétate d'éthyle | Césium restant ds. l'ac.d'éthy. | Facteur de décontamination |
|---|---|---|---|---|
| 10 ml contenant 8·6 mg DPCs | 2 ml HCl N/50 | non mesurable | $<2\gamma$ | >1000 |
| | 10 ml HCl N/50 | non mesurable | $<2\gamma$ | >1000 |
| | 10 ml HCl N/5 | non mesurable | $<2\gamma$ | >1000 |
| | 10 ml HCl N/2 | non mesurable | $<2\gamma$ | >1000 |

(B) *Courbe d'étalonnage*

Les courbes d'absorption ont été enregistrées en fonction de la concentration en DPA de la phase acétate d'éthyle (courbe I).

Le césium avait été extrait par une solution HCl 0·1 N. Les solutions de diverses

Tableau 2

| HCl | N | 0·5 N | | | 0·1 N | | | 0·05 N | 0·02 N | 0·01 N |
|---|---|---|---|---|---|---|---|---|---|---|
| pH | 0 | 0·3 | | | 1 | | | 1·3 | 1·7 | 2 |
| Durée agitation (min) | 3 | 3 | 15 | 30 | 3 | 15 | 30 | 3 | 3 | 3 |
| Durée décantation | 15 à 30 min | 30–45 min | 45 min | 60 min | 3–4 hr | | | 3–4 hr | 3–4 hr | 3–4 hr |
| Observations | pas d'émul. | pas d'émulsion | | | Décantation lente pas d'émulsion | | | Possibilité d'émul. ds.phase organique | | |

concentrations en DPA avaient été préparées par dilutions de la solution obtenue après extraction du césium. Il a été fait, de manière identique, deux séries de dilutions correspondant à deux précipitations différentes de DPCs. Quelques unes des valeurs obtenues sont données dans le Tableau 3, l'ensemble des résultats étant représenté sur les courbes (voir Figs. 1 et 2).

La loi de Beer n'est pas suivie dans tout le domaine de concentration étudié (Fig. 3), ce qui rend nécessaire une courbe d'étalonnage. Celle-ci peut être préparée aisément en dissolvant de la dipicrylamine dans de l'acétate d'éthyle et en la traitant, d'une manière identique aux essais par une solution chlorhydrique. Nous avons

Vol. 12 1959/6

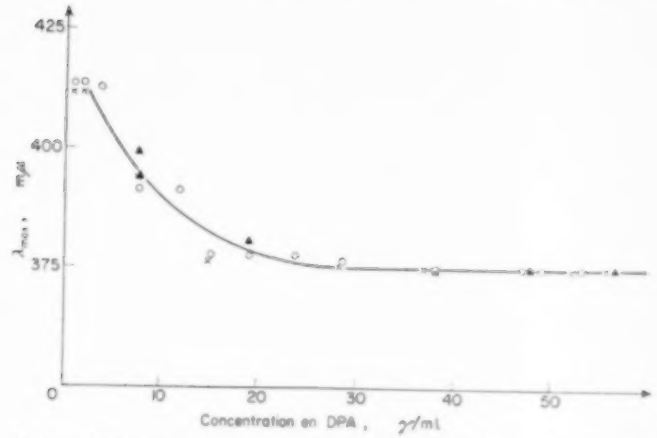



FIG. 1.—Variation de la longueur d'onde des maxima d'absorption en fonction de la concentration $\lambda_{max} = f(c)$.

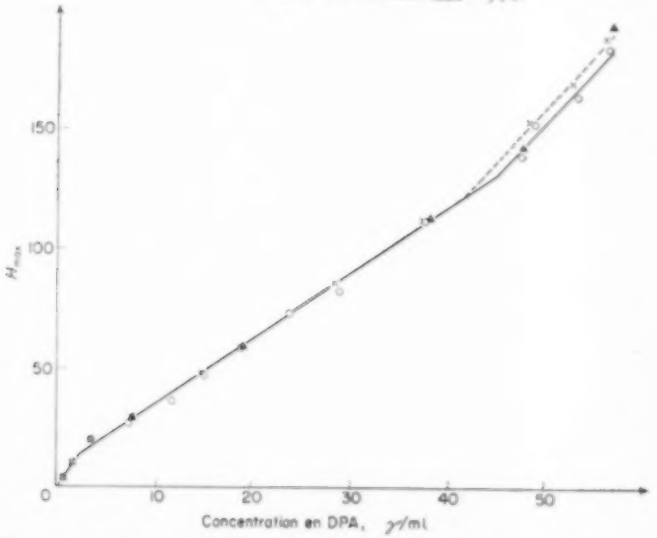
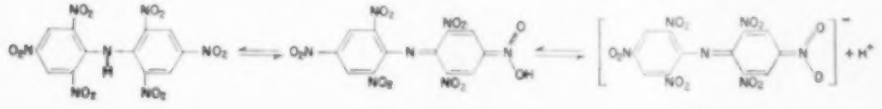



FIG. 2.—Variation de la hauteur du maximum d'absorption en fonction de la concentration

$$H_{max} = 2 \times 100 \left(1 - \frac{I}{I_0}\right) = f(c).$$

étudié différentes normalités de solutions d'extraction HCl 0·1 N–0·5 N et N. Les résultats obtenus ont été portés sur les courbes I et II, la concordance avec ceux obtenus après extraction de la DPCs est excellente. Ce qui semble prouver que l'on obtient dans les deux cas le même radical DPA après traitement à l'acide. KERTES et GOLDSCHMIDT[10] ont admis l'existence de plusieurs formes de la dipicrylamine:



I II III

TABLEAU 3

| | Concen. (DPA γ/ml) | Correspondant aux concentrations avant extraction | | Hauteur du maxi.d'absor- (unités arbitraires) | Longueur d'onde du max.d'abso. (mμ) | Précision du dosage (%) |
|---|---|---|---|---|---|---|
| | | (DPCs γ/ml) | (Cs γ/ml) | | | |
| | 47 | 36·1 | 10·95 | 139 ± 0·5 | 375 ± 1 | ±2 |
| 1e | 37·6 | 28·85 | 8·75 | 111·8 ± 0·5 | 375 ± 1 | ±2 |
| série | 23·5 | 18·02 | 5·47 | 73 ± 0·5 | 378 ± 2 | ±2 |
| essais | 18·8 | 14·4 | 4·38 | 58 ± 0·5 | 378 ± 2 | ±2 |
| | 7·52 | 5·77 | 1·75 | 27·2 ± 0·5 | 391 ± 2 | ±4 |
| | 48·4 | 37·1 | 11·25 | 152 ± 0·5 | 374 ± 1 | ±2 |
| 2e | 37·2 | 28·55 | 8·66 | 113 ± 0·5 | 375 ± 1 | ±2 |
| série | 27·9 | 21·4 | 6·49 | 85 ± 0·5 | 375 ± 1 | ±2 |
| essais | 14·9 | 11·4 | 3·46 | 47 ± 0·5 | 378 ± 2 | ±3 |
| | 7·44 | 5·71 | 1·73 | 29 ± 0·5 | 393 ± 3 | ±4 |

Vol. 12 1959/6

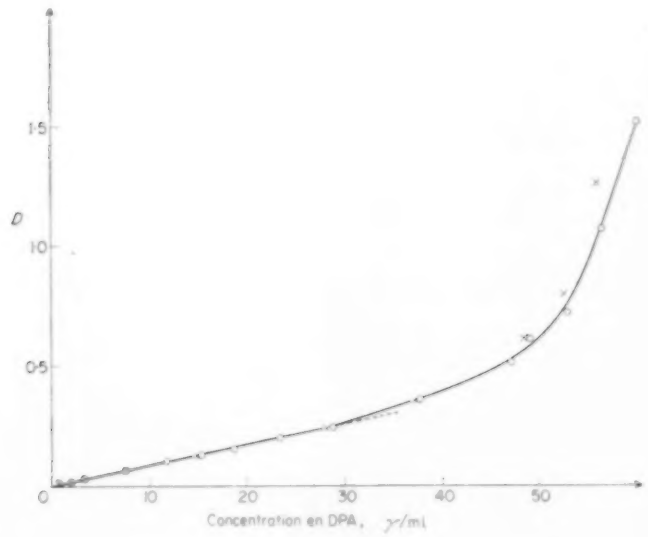



FIG. 3.

La forme (I), jaune, est insoluble dans l'eau, mais soluble dans les solvants non-polaire; la forme (II), rouge, se dissociant en (III) est un acide fort dont les sels sont solubles dans l'eau et les solvants organiques. Ce qui semble bien concorder avec les phénomènes de changement de coloration que nous avons observés lors de nos expériences. La variation de la hauteur du maximum d'absorption en fonction de la concentration en DPA (courbe II) est linéaire pour des concentrations en DPA comprises entre 5 et 40 $\gamma$/ml; en tenant compte de la longueur d'onde du maximum d'absorption (Fig. 1) et de la précision du dosage, la gamme optimum de concentration de la DPA pour effectuer la colorimétrie est de 15–35 $\gamma$/ml; les résultats seront alors reproductibles avec une précision de $\pm 2$ pour cent.

## V. MODE OPERATOIRE PROPOSE

Le césium entraîneur est ajouté à la solution à doser et celle-ci est traitée pour élimination des ions gênants. Les conditions de précipitation et de lavage ayant déjà été décrites, nous n'indiquerons ici que le mode opératoire concernant la colorimétrie.

(1) Mettre en solution dans l'acétate d'éthyle le précipité de DPCs à une concentration d'environ 200 $\gamma$/ml en césium, soit 660 $\gamma$/ml en DPA.

(2) Agiter pendant environ 3 min la solution obtenue en (1) avec un volume égal d'une solution chlorhydrique 0·5 N. Laisser décanter et séparer les deux phases claires.

(3) Ajuster la phase aqueuse et compter le radiocésium sur une aliquote de cette solution.

(4) Ajuster la phase organique et vérifier la décontamination sur une aliquote. Si la décontamination n'est pas totale, reprendre (2) sur un volume déterminé de (4).

(5) A partir de la solution obtenue en (4), préparer des dilutions contenant 15–35 $\gamma$/ml de DPA dans l'acétate d'éthyle. (facteurs de dilution compris entre 20 et 40)

(6) Préparer par ailleurs une solution étalon de la façon suivante: peser 33 mg de DPA, les dissoudre dans 50 ml d'acétate d'éthyle. Agiter 3 min cette solution avec 50 ml d'acide chlorhydrique 0·5 N. Décanter. Ajuster la phase organique comme en (4). Préparer des dilutions semblables à celles de (5) (ces solutions peuvent être conservées plusieurs jours).

(7) Effectuer la colorimétrie sur la longueur d'onde du maximum d'absorption, soit: 375 m$\mu$. Construire la courbe étalon à laquelle on comparera les valeurs obtenues pour le dosage. La précision est de $\pm 2$ pour cent pour l'ensemble du dosage colorimétrique. On détermine ainsi, en inactif, le rendement du dosage du radiocésium. Le comptage fait en (3) sera corrigé d'après cette valeur.

Vol. 12 9/60

J. Inorg. Nucl. Chem. 1960, Vol. 12, pp. 304 to 314. Pergamon Press Ltd. Printed in Northern Ireland

# SEPARATION OF CESIUM FROM FISSION PRODUCT WASTE SOLUTIONS

P. R. GRAY
Radiochemistry Laboratory, The Dow Chemical Company, Midland, Michigan

(*Received* 1 *May* 1959)

**Abstract**—A method is presented for separating cesium from a synthetic fission product solution. The fission products are converted to bromides with hydrobromic acid and concentrated by evaporation. Impure crystals of cesium molybdenyl pentabromide separate upon cooling. The final cesium bromide product (>99% CsBr, <1% RbBr) is obtained radiochemically pure in >95 per cent yield.

THE disposal of radioactive wastes from fissioned material is rapidly becoming a serious obstacle in the growth of atomic energy for domestic and industrial power. As our nuclear economy grows, large volumes of these fission product wastes will become available. Unless utilized in some manner, these wastes must be stored in expensive tanks for hundreds of years to allow sufficient time for the long-lived fission products, especially 27 year $^{137}Cs$ and 28 year $^{90}Sr$ to decay to safe radiation levels. If these two nuclides could be quantitatively removed from the waste solutions, the storage problems would be materially reduced. Besides reducing the storage problems, the removal of $^{137}Cs$ and $^{90}Sr$ would yield valuable radiation sources for medicine, industry, etc. Cesium-137[1] emits 0·514 MeV (92 per cent) and 1·176 MeV (8 per cent) $\beta$-particles and is essentially in equilibrium with a 0·662 MeV $\gamma$-ray from the internal conversion of 2·6 min $^{137m}Ba$. $^{90}Sr$ is a valuable $\beta$-energy source in that it emits no $\gamma$-rays and is in equilibrium with the 64·2 hr $^{90}Y$ which emits a 2·26 MeV $\beta$-particle.

Cesium bromide can be separated from its ores in a few relatively simple steps.[2] The ore is digested with hydrobromic acid, the gangue material removed and cesium bromide precipitated by the addition of isopropyl alcohol. High purity cesium bromide is obtained by the extraction of the precipitated cesium bromide into bromine.

It should be of interest to work out a similar procedure for the removal of radioactively pure cesium in high specific activity economically from fission wastes.

## EXPERIMENTAL

### *Materials*

A synthetic nitric acid fission product mixture was prepared using stable isotopes in amounts equal to the given concentrations of a typical waste fission product solution.[3] The fission product concentrations are based on the fission of $^{235}U$ and a reactor operation time of 42 days at a steady state reactor power of 500 MW. The cooling period is assumed to be 100 days. In addition to the fission product elements, the waste solutions contain some residual uranium not recovered during the reprocessing cycle as well as fuel element cladding and alloying materials and various corrosion products introduced during the reprocessing cycle.[4] The components and concentrations of the synthetic fission product solution are listed in Table 1.

[1] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).
[2] V. A. STENGER, U.S. Pat., 2 481 455 (1949).
[3] J. V. NEHEMIAS, R. C. DENNIS and E. AMBO, *University of Michigan College of Engineering Industry Programme Report IP-109*, January (1955).
[4] F. R. BRUCE, J. M. FLETCHER, H. H. HYMAN and J. J. KATZ (Editors), *Process Chemistry* p. 364. McGraw-Hill, New York (1956).



Vol. 12 1959/6

A few of the fission products were not added to the synthetic mixture, due to their unavailability or low concentrations required. These missing fission product elements are listed in Table 2.

Additional neodymium was added in place of several other trivalent rare earths, promethium, praseodymium, europium, and gadolinium, to insure the correct total rare earth content. The solution is made acidic with nitric acid, approximately 3–5 N. A high concentration of nitrate ion is assured by using aluminium nitrate, ferric nitrate, and uranyl nitrate as well as several other nitrates to introduce the correct composition of aluminium, iron, and uranium, etc.

TABLE 1.—COMPOSITION OF SYNTHETIC FISSION PRODUCT STOCK SOLUTION

| | | | |
|---|---|---|---|
| *Fission product elements* | | | |
| 5·14 g/l. | $ZrOCl_2 \cdot 8H_2O$ | or 1·45 g/l. | Zr |
| 3·90 g/l. | $Nd(NO_3)_3$ | or 1·70 g/l. | Nd |
| 4·44 g/l. | $(NH_4)_2Ce(NO_3)_6$ | or 1·14 g/l. | Ce |
| 1·90 g/l. | $La(NO_3)_3$ | or 0·47 g/l. | La |
| 0·61 g/l. | $Y(NO_3)_3$ | or 0·20 g/l. | Y |
| 1·32 g/l. | $Sr(NO_3)_2$ | or 0·55 g/l. | Sr |
| 0·86 g/l. | $Ba(NO_3)_2$ | or 0·45 g/l. | Ba |
| 0·26 g/l. | $RbNO_3$ | or 0·15 g/l. | Rb |
| 1·20 g/l. | Mo metal | or 1·20 g/l. | Mo |
| 0·07 g/l. | $NH_4I$ | or 0·05 g/l. | I |
| 1·93 g/l. | $RuCl_3$ hydrate | or <0·6 g/l. | Ru |
| 0·17 g/l. | $Sm_2O_3$ | or 0·15 g/l. | Sm |
| 0·16 g/l. | $TeO_2$ | or 0·13 g/l. | Te |
| 0·02 g/l. | $SbCl_3$ | or 0·01 g/l. | Sb |
| 0·04 g/l. | $Cd(NO_3)_2$ | or 0·02 g/l. | Cd |
| 0·04 g/l. | $SnCl_2$ | or 0·02 g/l. | Sn |
| 2·00 g/l. | CsBr | or 1·25 g/l. | Cs |
| *Fuel element cladding materials and corrosion products* | | | |
| 226·8 g/l. | $Al(NO_3)_3 \cdot 9H_2O$ | or 16·3 g/l. | Al |
| 219·0 g/l. | $Fe(NO_3)_3 \cdot 6H_2O$ | or 35·0 g/l. | Fe |
| 4·95 g/l. | $Ni(NO_3)_2 \cdot 6H_2O$ | or 1·0 g/l. | Ni |
| 0·96 g/l. | $CrO_3$ | or 0·5 g/l. | Cr |
| 0·80 g/l. | $Pb(NO_3)_2$ | or 0·5 g/l. | Pb |
| *Residual uranium* | | | |
| 90·72 g/l. | $UO_2(NO_3)_2 \cdot 6H_2O$ | or 43·0 g/l. | U |
| Nitric acid (~3–5 N). | | | |

The total weight of the stock solution components, exclusive of solvent is 567·3 g/l., of which cesium bromide constitutes 0·35 per cent of the solid weight. The fission products weigh 24·1 g or 4·2 per cent; the cladding materials, etc. weigh 452·5 g or 79·8 per cent and the residual uranium weighs 90·7 g or 16·0 per cent of the total.

Radioactive tracers were incorporated in the synthetic solution in several experiments to trace the radiochemical purity of the cesium. $\gamma$-Ray emitting isotopes of several of the more abundant fission products were used so that an analysis could be made without prior chemical separation steps. The radioactive tracers were obtained from the Oak Ridge National Laboratory. In Table 3 are given the radionuclear data for the isotopes considered.

Technical concentrated hydrobromic acid (48 per cent) was used.

*Methods of analysis*

Non-radioactive products were analysed routinely by X-ray fluorescence and X-ray diffraction. In one instance, cesium and molybdenum concentrations were determined by chemical quantitative analysis.

Radioactive products or aliquots were analysed on an Atomic Model 510 Single channel pulse height analyser, modified to allow automatic spectrum scanning. The sensing element was a 1¾ in. by 2 in. well-type cesium iodide (Tl) scintillation crystal mounted on a Dumont 6292 multiplier

TABLE 2.—FISSION PRODUCTS NOT ADDED TO THE SYNTHETIC FISSION PRODUCT SOLUTION

| Element | Concentration (g/l.) |
|---|---|
| Niobium | 0·03 |
| Technetium | 0·30 |
| Rhodium | 0·10 |
| Palladium | 0·05 |
| Selenium | 0·01 |
| Silver | <0·01 |
| Indium | <0·01 |

phototube. A cathode follower preamplifier preceded an Atomic Model 215 linear amplifier. The signal from the pulse height analyser was integrated by a Radiation Counter Laboratory Mark 15 Model 15 linear count-rate meter before being indicated on a standard 10 mV Brown strip chart recorder. A window width of 1V was used in obtaining the $\gamma$-ray spectra.

Vol. 12 1959/6

*Procedure and results*

A flow sheet of the process is given in Fig. 1. One thousand millilitres of the synthetic fission product solution was added to a 2 l., three-neck round bottom flask, fitted with a thermometer well.

TABLE 3.—RADIONUCLIDES ADDED TO THE SYNTHETIC FISSION PRODUCT MIXTURE

| Radionuclide | Half-life[1] | Energy of prominent[1] $\gamma$-rays |
|---|---|---|
| $^{137}$Cs | 26·6 years | 0·662 MeV |
| $^{95}$Zr–$^{95}$Nb | 65 days ($^{95}$Zr) | 0·722 MeV, 0·754 MeV ($^{95}$Zr) |
| | 35 days ($^{95}$Nb) | 0·765 MeV ($^{95}$Nb) |
| $^{144}$Ce–$^{144}$Pr | 285 days ($^{144}$Ce) | 0·134 MeV ($^{144}$Ce) |
| | 17·3 min ($^{144}$Pr) | |
| $^{106}$Ru–$^{106}$Rh | 1·00 year ($^{106}$Ru) | |
| | 30 sec ($^{106}$Rh) | 0·513 MeV, 0·624 MeV ($^{106}$Rh) |

In the "hot" experiments containing radioactive tracers, an aliquot of a tracer solution containing standardized $^{137}$Cs, $^{95}$Zr–$^{95}$Nb, $^{144}$Ce–$^{144}$Pr and $^{106}$Ru–$^{107}$Rh tracer was added also. Five hundred millilitres of technical hydrobromic acid (48 per cent) was added and heating (by a 2 l. heating mantle) begun slowly. The effluent bromine and nitrogen oxide vapours were passed through a water condenser and the noncondensibles were bubbled through a caustic solution. When the bromine effluence ceased, additional hydrobromic acid was cautiously added. A total of 1800 ml of concentrated hydrobromic acid was generally sufficient to destroy the nitrates present and convert

the cations to bromides. An additional 700 ml of hydrobromic acid was added to increase the acid concentration. Concentration of the solution was continued until a final volume of 300–1000 ml was attained. The reducing atmosphere of the hydrobromic acid prevents the ruthenium from escaping from the system as the tetroxide and negates the necessity of prior ruthenium removal.

Upon cooling, reddish-brown crystals separated from the solution. These crystals were readily removed by centrifugation and washed with 100 ml of concentrated hydrobromic acid. These reddish-brown crystals were found to contain most of the cesium, as well as ruthenium, bromine,

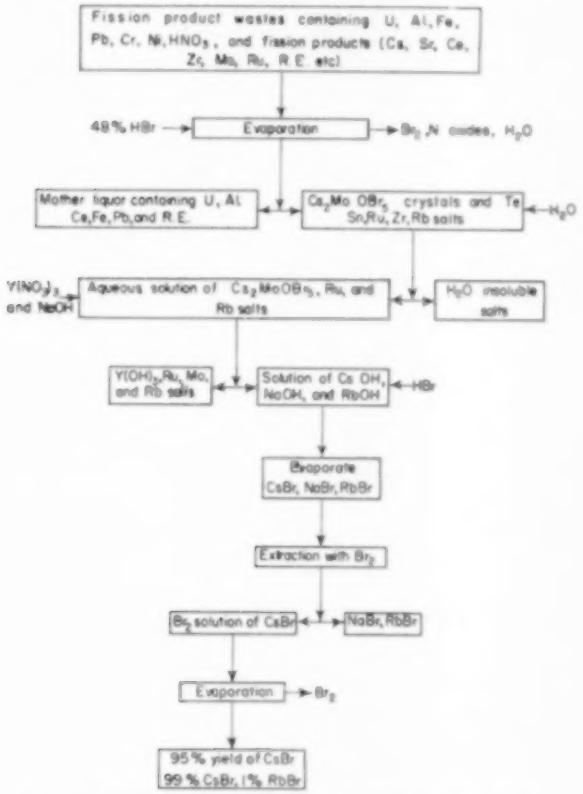

Fission product wastes containing U, Al, Fe, Pb, Cr, Ni, $HNO_3$, and fission products (Ca, Sr, Ce, Zr, Mo, Ru, R.E. etc)
48% HBr
Evaporation
$Br_2$, N oxides, $H_2O$
Mother liquor containing U, Al, Ca, Fe, Pb, and R.E.
$Cs_2MoOBr_5$ crystals and Te, Sn, Ru, Zr, Rb salts
$H_2O$
$Y(NO_3)_3$ and NaOH
Aqueous solution of $Cs_2MoOBr_5$, Ru, and Rb salts
$H_2O$ insoluble salts
$Y(OH)_3$, Ru, Mo, and Rb salts
Solution of Cs OH, NaOH, and RbOH
HBr
Evaporate CsBr, NaBr, RbBr
Extraction with $Br_2$
$Br_2$ solution of CsBr
NaBr, RbBr
Evaporation
$Br_2$
95% yield of CsBr
99% CsBr, 1% RbBr

FIG. 1.—Separation of cesium from fission product waste solutions.

and molybdenum, and small amounts of cerium and zirconium. Water leaching of the crystals with 100 ml water solubilized the cesium, resulting in a cherry-red supernatant solution, which was separated from the white residue by centrifugation. The white residue was found to contain the cerium and zirconium while the cesium, molybdenum, ruthenium, and bromine were in the red solution.

The ruthenium and molybdenum were removed from the solution by the addition of NaOH after adding a suitable carrier such as iron or yttrium. This hydroxide precipitate removes the molybdenum as well as most of the ruthenium. The hydroxide treatment did, however, introduce a considerable quantity of sodium. After acidifying with hydrobromic acid the supernatant solution was evaporated to dryness. Cesium was separated from the large sodium bromide content by extracting cesium bromide into bromine. About 40 ml of bromine were used for the initial extraction and the residue after filtering was washed with an additional 20 ml of bromine. The cesium bromide was recovered by the evaporation of the bromine. The chemical purity of the cesium bromide was increased slightly by dissolving the cesium bromide in 2–3 ml water, filtering, and adding 40 ml isopropyl alcohol to

the supernate. The cesium bromide precipitate was washed once with 20 ml isopropyl alcohol and dried at 110°C.

The prime crystals obtained on the evaporation of the fission product solution were found to be composed mainly of a cesium–molybdenum–bromine complex, cesium molybdenyl pentabromide, $Cs_2MoOBr_5$, and possibly a cesium–ruthenium–bromine compound, probably $Cs_2RuBr_5$.

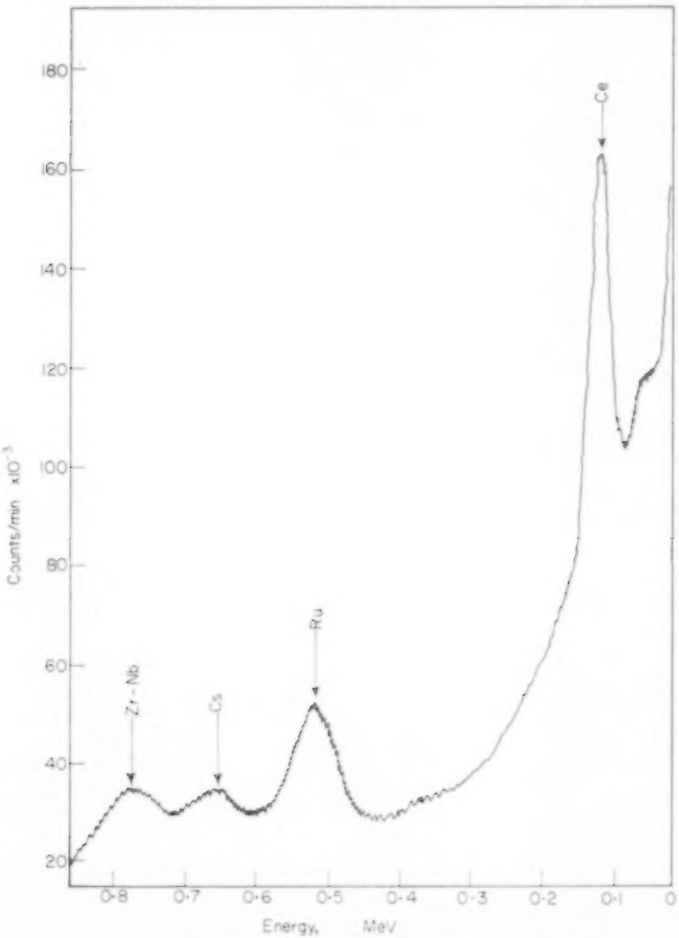



FIG. 2.—$\gamma$-Spectrum of fission product starting solution.

Figs. 2, 3, 4 and 5 illustrate the recovery and decontamination of radioactive cesium. Fig. 2 is a $\gamma$-spectrum of the original fission product solution to which standardized $^{144}Ce$–$^{144}Pr$, $^{106}Ru$–$^{106}Rh$ $^{95}Zr$–$^{95}Nb$ and $^{137}Cs$ tracers had been added. Fig. 3 is a $\gamma$-spectrum of the impure crystals of $Cs_2MoOBr_5$ obtained after the initial evaporation, Fig. 4 is a $\gamma$-spectrum of the final cesium bromide product, and for comparison, Fig. 5 is a $\gamma$-spectrum of the $^{137}Cs$ tracer used. The cesium bromide product appears to be radioactively pure cesium, as evidenced by the removal of the $^{144}Ce$–$^{144}Pr$, $^{106}Ru$–$^{106}Rh$ and $^{95}Zr$–$^{95}Nb$ activities. The specific activity of the cesium in the starting solution was 60,000 counts/min per g CsBr, and the specific activity of the cesium in the CsBr product is 60,150 counts/min per g CsBr, indicating a quite pure product.

$\gamma$-Spectra obtained during various stages of the process indicate that the combined mother liquor hydrobromic acid supernate and hydrobromic acid washings of the impure $Cs_2MoOBr_5$ crystals

Vol. 12 1959/6

contain essentially all the cerium, most of the zirconium, and smaller amounts of ruthenium and cesium. The water insoluble residue remaining after the leaching of the $Cs_2MoOBr_5$ crystals appears to be radioactively pure $^{95}Zr$. However, it is believed that other fission product activities not used in these experiments would contaminate this residue. For example, tellurium was found to be present in this zirconium rich fraction by X-ray fluorescence, and 115 day $^{127m}Te$ present in fission products could be expected to concentrate here.

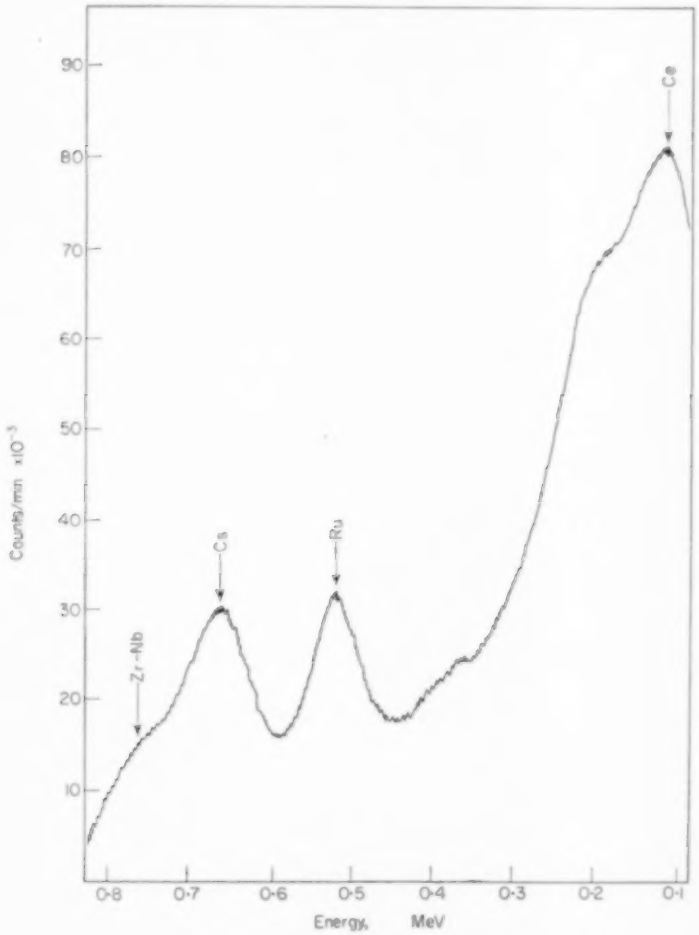



FIG. 3.—$\gamma$-Spectrum of impure $Cs_2MoOBr_5$ crystals.

Only 66 per cent of the cesium bromide was recovered in the above experiment. About 5 per cent of the cesium bromide was not extracted into the bromine from the CsBr–NaBr phase. This may be recoverable by a second bromine extraction. Most of the residual cesium (29 per cent of the original appears to have been retained in the mother liquor, i.e., it did not crystallize as hydrobromic acid insoluble $Cs_2MoOBr_5$. However, in this experiment, the evaporation concentration of the fission product solution was stopped when the volume was 1000 ml and the solution boiling point 130–135°C. Other experiments have indicated that concentrating the solution to a final volume of 300 ml and a temperature of 150°C, resulted in over 95 per cent recovery of the cesium. The purity of $Cs_2MoOBr_5$ crystals is decreased accordingly, but this is not expected to affect the subsequent purification of the cesium bromide materially.

The chemical purity of the cesium bromide product was determined in an experiment in which no tracer activity was introduced. While specific activity data on the tracer experiments indicated that the chemical purity of the product was quite good, additional direct evidence from a "cold" experiment was obtained by an analysis of the product by X-ray fluorescence. The cesium bromide product was found to be greater than 99 per cent pure, the only impurity found by X-ray analysis being a small amount of rubidium. Rubidium contamination is not considered serious in the cesium product,

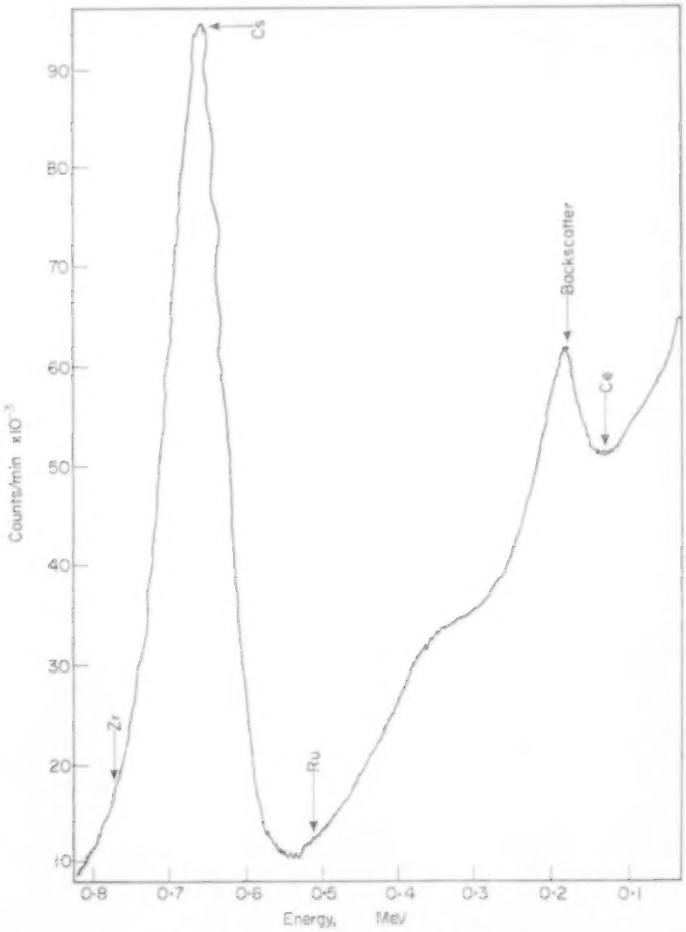



FIG. 4.—$\gamma$-Spectrum of cesium bromide product.

however, since $^{86}$Rb, formed in fission in only $10^{-6}$ per cent yield has a half-life of 18·7 days and $^{87}$Rb, which has a fission yield of 2·7 per cent and a half-life of $5 \times 10^{10}$ years has no $\gamma$-activity associated with it. Moreover, most of the rubidium has been removed in the process. The decontamination factor for the rubidium removal is ~25, indicating less than 2 per cent of the original rubidium is retained in the product.

The yield of cesium can be appreciably improved by the addition of isopropyl alcohol to the mother liquor after the crystallization of the impure $Cs_2MoOBr_5$. Cesium bromide as well as $Cs_2MoOBr_5$ is insoluble in isopropyl alcohol, whereas many other metallic bromides are quite soluble. The alcohol addition therefore precipitates additional $Cs_2MoOBr_5$ and any uncomplexed cesium bromide. The specific activity of these alcohol crystals is not as high as the prime crystals

of impure $Cs_2MoOBr_5$. In an experiment designed to determine the yield of these crystallizations and precipitations it was found that 63·8 per cent of the cesium-137 activity was recovered in the impure $Cs_2MoOBr_5$ crystals (total crystal weight = 2·7998 g). An additional 35·3 per cent of the $^{137}Cs$ activity precipitated upon the addition of 3·5 l. of isopropyl alcohol to the 1615 ml of combined mother liquor and prime crystal washings. (weight = 6·610 g). This indicates a total recovery of 99·1 per cent of the cesium in a total solid weight of 9·410 g or solids which were 13·1 per cent cesium

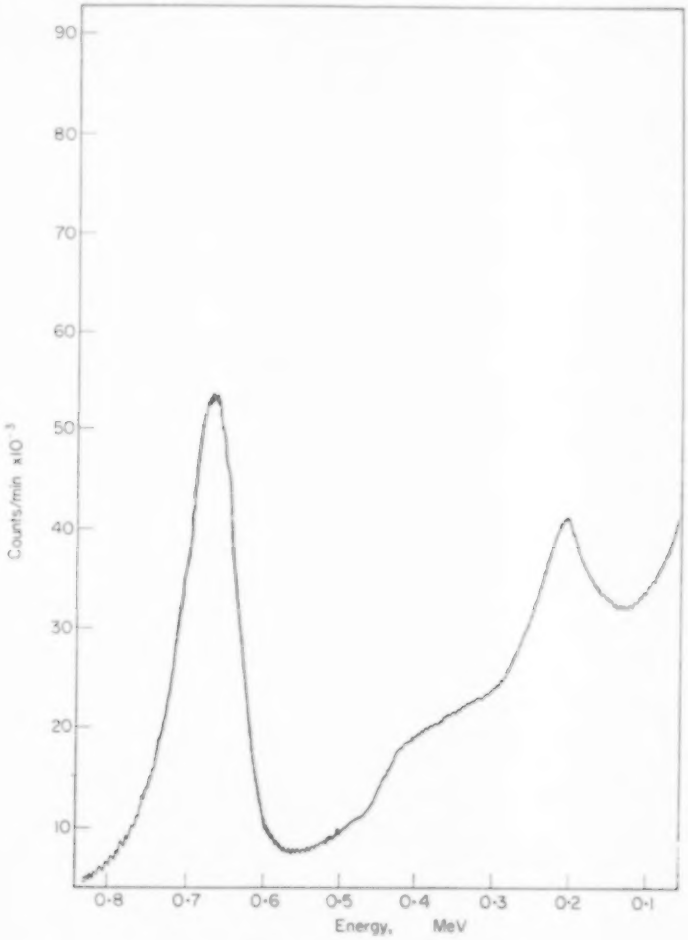



FIG. 5.—$\gamma$-Spectrum of $^{137}Cs$ tracer.

on a weight basis. In all 98·8 per cent of the cesium was leached with water from the impure $Cs_2MoOBr_5$ prime crystals and 97·7 per cent of the cesium was leached from the alcoholic crystals. The total solid weight of the evaporated combined leachings was 6·2313 g or 19·5 per cent cesium by weight. While this particular experiment was not continued to the final recovery of cesium bromide, it is anticipated that no undue difficulties would be encountered.

*Identification of the complex cesium crystals as* $Cs_2MoOBr_5$

Pure crystals of the complex were prepared by a method identical to the treatment afforded the fission products. Twenty grammes of cesium bromide were dissolved in water and added to a solution containing 12 g of molybdenum metal dissolved in aqua regia. Nitric acid was added and evaporation

of the solution was begun with the simultaneous slow addition of technical hydrobromic acid (48 per cent). Heating and evaporation were continued until all the nitrates present were destroyed and the solution quite concentrated. Upon cooling, red crystals of the complex cesium salt separated and were removed by centrifugation. The crystals were washed once with hydrobromic acid and dried after washing with isopropyl alcohol.

Several independent pieces of information support the identification of the formula of the cesium complex crystals as $Cs_2MoOBr_5$. After X-ray fluorescence had identified the complex as containing cesium, molybdenum and bromine and reported a bromine content of 52·8 per cent, a micro analysis of the cesium and molybdenum content was made. These analyses, together with the elemental analysis of $Cs_2MoOBr_5$ and $Cs_2MoBr_6$ for comparison, are given in Table 4.

TABLE 4.—CHEMICAL ANALYSES OF $Cs_2MoOBr_5$ CRYSTALS

| Element | Reported analysis (%) | $Cs_2MoOBr_5$ (%) | $Cs_2MoBr_6$ (%) |
|---|---|---|---|
| Cs | 33·4–35·6 (Microchemical)* | 34·20 | 31·60 |
| Mo | 12·37 (Microchemical) | 12·34 | 11·41 |
| Br | 52·8 (X-ray fluorescence) | 51·40 | 57·00 |
| O | — | 2·06 | — |

* The range reported for the cesium is attributed to the lack of a good quantitative analysis method.

X-Ray diffraction measurements on the crystals identified them to be face centred cubic belonging to the $K_2PtCl_6$ type compounds. Since the chemical analyses apparently preclude a $Cs_2MoBr_6$ formula, other formula possibilities were investigated. The oxidation state of the molybdenum was determined by two separate experiments. A permanganate titration of an aqueous solution of the crystals after quantitatively removing the bromine by the addition of silver sulphate established a value of 0·996 for the electron change of the molybdenum during the oxidation, an indication that the molybdenum was originally present as a pentavalent ion. This was confirmed by a polarographic analysis of the crystals. A polarogram was obtained from a sample dissolved in 0·3 N hydrochloric acid. A wave was found having a half-wave potential of −0·69 V corresponding to the reduction from +5 to +3. A sample of sodium molybdate analysed in the same electrolyte gave pronounced half-waves at −0·2 V for the +6 to +5 reduction and at −0·71 V for the +5 to +3 reduction. The molybdenum in the complex has an oxidation state of +5, since little or no wave was produced in the −0·2 V region.

The identification of the oxidation state of the molybdenum as +5, suggested the possibility of the $Cs_2MoOBr_5$ formula. The presence of oxygen in the crystal was confirmed by infra-red analysis. A bond was identified at 10·51 $\mu$, that is, 952 $cm^{-1}$ which is in the region expected for a Mo–O bond. No bonds were found corresponding to multiple oxygen linkages. From these sets of evidence, the crystals have been characterized as $Cs_2MoOBr_5$.

$Cs_2MoOBr_5$ is soluble in water, forming a cherry red solution. The crystals are insoluble in concentrated hydrobromic acid and isopropyl alcohol.

Crystals of $Cs_2MoOBr_5$ can be made in the absence of nitric acid, also. A solution was prepared containing cesium bromide in water, molybdic acid, principally as ammonium molybdate and concentrated hydrobromic acid. After heating to concentrate the solution, with additional hydrobromic acid being added to maintain a high acid content, red crystals, identified as $Cs_2MoOBr_5$ separated on cooling. Yields of $Cs_2MoOBr_5$ of 99 per cent have been obtained by this method as well as starting with molybdenum metal in a nitric acid system.

Quite possibly, some of the cesium from the original evaporation and concentration of the fission product solutions crystallizes as a cesium–ruthenium–bromine complex. This is suggested by the relatively large ruthenium content of the impure crystals. In order to establish the existence and relative insolubility of such a cesium–ruthenium–bromine complex, ruthenium trichloride hydrate and cesium bromide were dissolved in water. Nitric acid was added and the solution was concentrated and evaporated with the simultaneous addition of hydrobromic acid. After cooling, dark brown

Vol. 12 1959/6

crystals separated, which were subsequently identified by X-ray fluorescence as containing cesium, ruthenium and bromine in approximately the same ratio as the cesium, molybdenum and bromine in $Cs_2MoOBr_5$. The crystals were not identifiable by X-ray diffraction, but were possibly hexagonal. These might suggest a $Cs_2RuBr_5$ formula. No further experiments were done to identify these ruthenium crystals.

## DISCUSSION

Cesium molybdenyl pentabromide, $Cs_2MoOBr_5$, was reported in 1905 by WEINLAND and KNÖLL[5] who prepared the complex by using Mo : Cs concentrations in the proportion 2 : 1. A solution of molybdenum trioxide in HBr was reduced electrolytically to +5. The resulting pentavalent molybdenum solution was transferred under a nitrogen atmosphere to an air-free flask containing a solution of cesium bromide. The resulting garnet-red octahedral cesium molybdenyl pentabromide crystals were washed with hydrobromic acid, drained and dried in vacuum.

It would appear that the complex can be prepared much more easily; the pentavalent molybdenum being obtained by the reducing atmosphere of hydrobromic acid. In the presence of cesium bromide in the same solution, cesium molybdenyl pentabromide crystallizes upon cooling. The complex is quite stable in air, no oxidation to hexavalent molybdenum being noted.

Since nitric acid is not necessary in the preparation of the complex salt, as evidenced by the preparation of cesium molybdenyl pentabromide in the absence of nitric acid or nitrates using ammonium molybdate, cesium bromide and hydrobromic acid, the removal of nitric acid from the fission product solutions by solvent extraction, reaction with formaldehyde, etc., would reduce the amount of free bromine and nitrogen oxide vapours during the evaporation and concentration with hydrobromic acid. The bromine vapours can be condensed and if not contaminated by entrainment of the fission product solution can be used for the extraction of the cesium bromide product.

The separation of the cesium as cesium molybdenyl pentabromide from the concentrated hydrobromic acid solution necessitated a modification of the original plan to precipitate cesium bromide with isopropyl alcohol. The recovery of cesium in the impure cesium molybdenyl pentabromide crystals has been only 60–70 per cent. Yields of greater than 99 per cent should be possible by further concentration of the solution, as it has been demonstrated that greater than 99 per cent of the cesium crystallizes from the solution as $Cs_2MoOBr_5$ when the solution becomes sufficiently concentrated. However, the yield of cesium can be raised also, by a second precipitation of cesium molybdenyl pentabromide and uncomplexed cesium bromide by the addition of isopropyl alcohol. In this manner, greater than 99 per cent of the cesium was removed from the fission product solution giving a mixture of cesium compounds ($Cs_2MoOBr_5$, CsBr, possibly a cesium–ruthenium–bromide complex, etc.) with a cesium content of 13·1 per cent. (Original cesium content of the fission product solution was 0·22 per cent.) Water leaching of these precipitated solids increased the cesium content to 19·5 per cent.

While the recovery of cesium is not complete enough to materially improve the waste fission product storage problem, it might be possible to repeat the cesium separation from the mother liquor. Inactive cesium and molybdenum must be added and the evaporation and concentration repeated. Three such repetitions of the cesium

[5] R. F. WEINLAND and W. KNÖLL, *Z. Anorg. Chem.* **44**, 81 (1905).

separation would theoretically reduce the cesium to only $10^{-6}\%$ of the original cesium content. The specific activity of these separated cesium fractions would probably be too low to be useful as radiation sources.

The specific activity of the cesium product could be increased by conversion of the cesium bromide (62·4% cesium) to other salts such as cesium chloride (78·9% cesium), etc.

*Acknowledgements*—The author wishes to express his appreciation for technical assistance provided by J. IFFT and D. H. CLAREY of this laboratory and X-ray analyses by P. P. NORTH and H. W. RINN, infra-red analysis by R. A. NYQUIST and polarographic analysis by O. L. DANIELS.

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 315 to 326. Pergamon Press Ltd. Printed in Northern Ireland

# THE EXTRACTION OF NITRIC ACID AND THORIUM NITRATE BY TRI-n-OCTYLPHOSPHINE OXIDE IN CYCLOHEXANE

R. A. ZINGARO* and J. C. WHITE
Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(*Received* 17 *March* 1959; *in revised form* 28 *May* 1959)

**Abstract**—The distribution of nitric acid and thorium(IV) nitrate between aqueous solutions and solutions of tri-n-octylphosphine oxide in cylcohexane has been examined as a function of temperature and various extraction variables at constant aqueous ionic strength. Up to a maximum concentration of 0·4 M, the distribution behaviour of nitric acid was found to be consistent with first power dependency on the organic reagent concentration. In the case of acidic thorium nitrate solutions, provided the concentration of both thorium(IV) and hydrogen ion are maintained below 0·01 M, the extraction of the metal as $Th(NO_3)_4 \cdot 3TOPO$ is indicated. At higher concentrations the formation of organic adducts containing both the metal nitrate and nitric acid takes place. The temperature dependency of the extraction is very small in the case of the acid extraction and too slight in the case of thorium nitrate to be observed by the analytical methods used. During the course of these studies the solubility and density of saturated tri-n-octylphosphine oxide solutions in cyclohexane in the temperature range of 6·5–35°C was also measured.

Vol. 12 59/60

IN recent communications[1] the selectivity and versatility of tri-n-octylphosphine oxide (hereinafter referred to as TOPO) as a reagent for the solvent extraction of various metals has been reported. These workers observed that thorium(IV) is readily extracted by TOPO in cyclohexane from aqueous nitrate or chloride solutions, but only very weakly from sulfate solutions. The primary purpose of the foregoing studies was to obtain information that would be useful principally for analytical applications. The present study represents one of the initial efforts undertaken for the purpose of obtaining a more fundamental understanding of the nature of the extraction processes involving TOPO.

In this investigation the distribution of nitric acid and of thorium(IV) nitrate between acidic nitrate solutions (of ionic strength 2 M) and cyclohexane solutions of TOPO was measured as a function of temperature and several extraction variables.

In order to avoid the use of organic solutions which might be too concentrated as a result of the decreased solubility at the lower temperatures, the solubility of TOPO in cyclohexane at 6·5°C, 11°C, 25°C and 35°C was measured as well as the densities of these solutions.

## EXPERIMENTAL

*Tri-n-octylphosphine oxide*. The TOPO reagent was prepared by purification of the Eastman white label product. This involved initial oxidation in petroleum ether solution with aqueous potassium

* Chemistry Department, A. and M. College of Texas, College Station, Texas.

[1] W. J. ROSS and J. C. WHITE, [a] ORNL-CF-56-9-18 (1956); [b] ORNL-2326 (1957); [c] ORNL-2382 (1957); [d] ORNL-2453, p. 68 (1957); [e] ORNL-2498 (1958); [f] ORNL-2627, (1958); [g] C. K. MANN and J. C. WHITE, *Analyt. Chem.* **30**, 989 (1958); [h] C. A. HORTON and J. C. WHITE, *Ibid.* **30**, 1779 (1958); [i] J. P. YOUNG and J. C. WHITE, *Ibid.* **31**, 393 (1959).

permanganate in order to oxidize any phosphinous acids to the corresponding phosphinic acids. Manganese compounds were then removed by successive treatment with sodium oxalate and sulphuric and hydrochloric acids. The petroleum ether solution of TOPO was then slurried with activated alumina to remove the phosphinic acids. The final product, recrystallized from petroleum ether at −20°C, contained a maximum of 0·07 per cent of phosphinic acids as indicated by titration and the ultra-violet spectrum. The melting point of the purified TOPO was 53·5°C.

*Cyclohexane.* Eastman white label grade cyclohexane was used without further purification.

*Thorium nitrate.* An aqueous solution of reagent grade thorium nitrate was adsorbed on Dowex-50 resin which was eluted with hydrochloric acid to remove the rare earths. Thorium(IV) was finally eluted with sulphuric acid and precipitated as thorium oxalate. The oxalate was ignited to the oxide at 1000°C and subsequently dissolved in nitric acid and evaporated to crystals of $Th(NO_3)_4 \cdot 4H_2O$.

*Solutions.* Stock solutions were prepared at each temperature from reagent grade chemicals or from reagents purified as previously described. Less concentrated solutions were prepared by dilution of the stock solutions. Sufficient sodium nitrate was added to all aqueous solutions to adjust the ionic strength to 2 M. All solutions were analysed prior to equilibration.

TOPO–Cyclohexane solutions were prepared by weighing calculated quantities of the solute and diluting with appropriate amounts of the solvent at the given temperature.

*Temperature control.* The 11°C-, 12°C- and 25°C-constant temperature baths were controllable to within ±0·05°C. The 35°C-bath was controlled to within ±0·2°C. The 6·5°C-measurements were made in an equilibrium mixture of cyclohexane at its freezing point (6·5°C). A cyclohexane slush was maintained at its equilibrium temperature by immersion in a second bath of frozen cyclohexane, the temperature of which was controlled by a third removable surrounding ice-water bath. The temperature fluctuation in the cyclohexane slush was ±0·1°C.

*Solubility and density measurements.* Cyclohexane was saturated with TOPO at a temperature higher than that at which the determination was to be made. The saturated solution was then equilibrated by shaking in a constant temperature bath. Samples were withdrawn through cotton filters into calibrated pipettes and weighed in glass-stoppered weighing bottles. The solution was then evaporated at temperatures below the boiling point of the solvent and final traces of cyclohexane were removed *in vacuo* at temperatures above its boiling point. The weight of dissolved solute was then obtained.

A minimum of four samples was measured at each temperature; the maximum deviation within a series of measurements was 0·5 per cent. The rate of equilibrium was very slow at 35°C; reproducible measurements were obtained only after continual shaking for 48 hr. Attempts to make these measurements at 45°C were unsuccessful in that the results were not reproducible. At the lower temperatures equilibrium was reached after an hour.

*Extraction measurements.* Equal volumes (usually 20 ml) of aqueous and organic solutions of known composition were equilibrated by rapid shaking in glass separatory funnels for at least 2 hr at 35°C and 8 hr at the lower temperature. Analysis of control samples at each temperature at fixed time intervals showed that equilibrium was reached after 10–20 min. Following equilibration, the phases were separated and samples were taken for analysis.

Previous studies[2] showed that there was no detectable transfer of sodium nitrate or nitric acid into pure cyclohexane and that no water of hydration is associated with either the free TOPO solutions or the TOPO–thorium complexes.

*Analyses.* In the case of the pure nitric acid–sodium nitrate solutions, the total acidity of the aqueous phase was directly determined by titration using phenolphthalein indicator. The organic solutions were dissolved in ethanol and titrated in this solvent. When thorium was present, potassium oxalate was first added to complex the thorium and the acid was then titrated. In the latter case a blank correction was also made. The blank corresponded in composition to the sample, except that no acid was present.

When present in sufficient concentration, thorium was determined gravimetrically by precipitation as the oxalate and ignition to the oxide. In the majortiy of cases, thorium in both phases was determined colorimetrically[3] following equilibration.

[2] W. J. Ross. Unpublished results.
[3] P. F. THOMASON, M. A. PERRY and W. M. BYERLY, *Analyt. Chem.* **21**, 1239 (1949).

Vol. 12 1959/6

## RESULTS AND DISCUSSION

### *Solubility of* TOPO *in cyclohexane*

The density and the composition of saturated TOPO–cyclohexane solutions are given in Table 1.

It is noted that the solubility of TOPO in cyclohexane increases by four and half times as the temperature increases from 6·5 to 25°C. Concurrently, the density increases, although the change is small. As the temperature is increased from 25°C to 35°C, the solubility increases only very slightly. It is also to be noted that there is a very slight decrease in density at 35°C compared with the value at 25°C.

TABLE 1.—DENSITY AND SOLUBILITY OF SATURATED TOPO–CYCLOHEXANE SOLUTIONS AT VARIOUS TEMPERATURES

| Temperature (°C) | Density (g/l.) | Solubility TOPO | | Composition % TOPO by wt | Mole fraction | |
|---|---|---|---|---|---|---|
| | | (g/l). | (mole/l.) | | TOPO | Cyclohexane |
| 6·5 | 0·7711 | 81·42 | 0·2107 | 10·56 | 0·02505 | 0·9749 |
| 11·0 | 0·7912 | 164·9 | 0·4253 | 20·78 | 0·05402 | 0·9458 |
| 25·0 | 0·8057 | 356·1 | 0·9222 | 44·20 | 0·1471 | 0·8530 |
| 35·0 | 0·7977 | 360·8 | 0·9334 | 45·24 | 0·1690 | 0·8310 |

### *Extraction of nitric acid*

In the treatment of the nitric acid extraction data, it is assumed that TOPO extracts nitric acid according to the following equilibrium:

$$H^+_{(a)} + NO^-_{3(a)} + n\text{TOPO}_{(o)} \rightleftharpoons (HNO_3 \cdot n\text{TOPO})_{(o)}. \quad (1)$$

Although $n$ is expected to be a small, integral number, it may be smaller than one if more than a mole of nitric acid is extracted for each mole of TOPO, or, if polymerization occurs in the organic phase, $n$ may have a fractional value. It is also necessary to assume that TOPO exists as the monomer* in cyclohexane solution. Since the ionic strength of all solutions is 2 M, and if only those experiments are considered in which the total quantity of acid extracted is less than 0·05 mole, the concentration of nitrate ion will remain essentially constant at 2 M. Let us define the extraction coefficient, $E_a^o$, as follows:

$$E_a^o = \frac{(HNO_3 \cdot n\text{TOPO})_o}{(H^+)_a} = \frac{\text{nitric acid concentration of organic phase}}{\text{nitric acid concentration of aqueous phase}} \quad (2)$$

The equilibrium quotient can be approximated by the following expression:

$$K = \frac{(HNO_3 \cdot n\ \text{TOPO})_o}{(H^+)_a(NO_3^-)_a(\text{TOPO})_o^n} = E_a^o/2(\text{TOPO})_o^n \quad (3)$$

According to equation (3), a plot of log $E_a^o$ against log $(\text{TOPO})_o$ should yield a straight line of slope $n$. Such plots were made using experimentally determined values of $E_a^o$

* C. F. BAES of the Oak Ridge National Laboratory, in some recent isopiestic investigations of solutions of TOPO in n-hexane, has found no evidence of polymerization. This information was obtained by personal communication.

and calculating $(TOPO)_o$, i.e., the concentration of uncomplexed organic reagent, by difference. A series of plots was obtained using values of $(TOPO)_o$ calculated for $n = 0{\cdot}5$, 1 and 2. The only reasonable correlation was obtained for $n = 1$. A plot

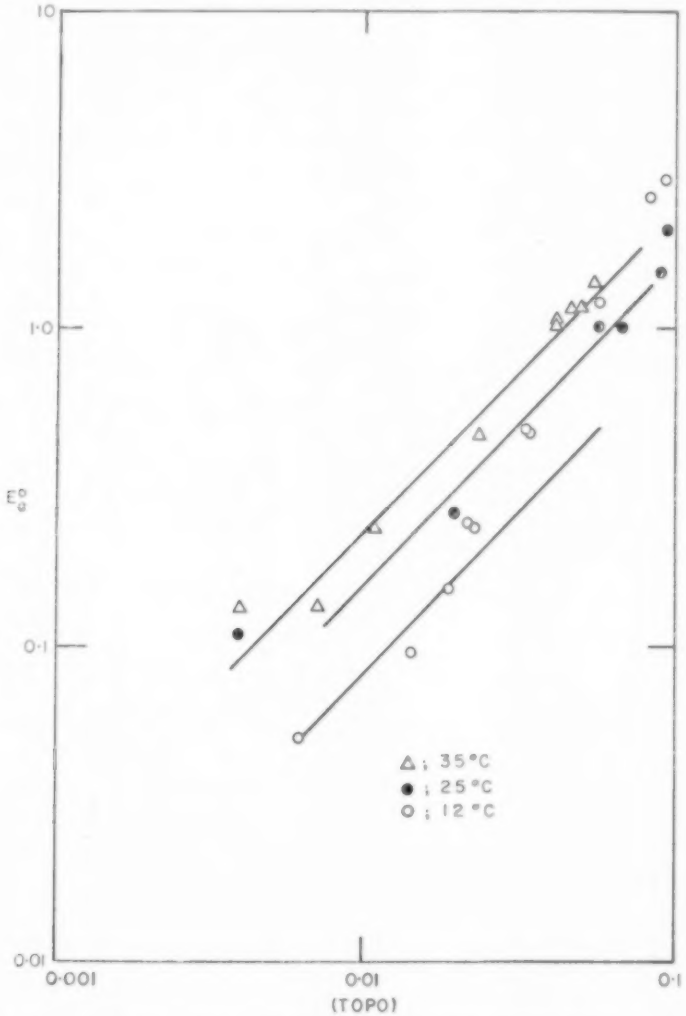



FIG. 1.—Distribution of nitric acid between water and cyclohexane as a function of equilibrium TOPO concentration.

of $E_a^o$ vs. $(TOPO)_o$ (for $n = 1$) is shown in Fig. 1 at the various temperatures. The lines have been drawn with a slope of unity. It is seen that the extraction coefficients decrease slightly with decreasing temperature, although the three uppermost points at 12·4°C are well above those at 25°C. This may be due in part to experimental error ($(H^+) \sim 0{\cdot}001$ in this region); however, these points fall on a steeper slope and indicate a dependency on $n > 1$.

The 12·4°C data were also plotted using $(TOPO)_o$ values based on the assumed

Vol. 12 1959/6

formation of a $HNO_3 \cdot 2TOPO$ complex. These lines fell on a slope of 0·5. This indicates that other equilibria are involved in the more dilute solutions at lower temperatures and that the assumption of the formation of a single complex is inadequate.

At 25°C and 35°C the lowest points of Fig. 1 are out of line, but in this region the hydrogen ion concentration is sufficiently high so that the organic reagent is essentially 100 per cent saturated and values of the organic reagent concentration calculated by difference are subject to considerable error.

In the region of $(H^+)_a = 0{\cdot}005$ to 0·4 M and TOPO = 0·01 to 0·05 M, the extraction behaviour is reasonably consistent with first power dependency on the organic reagent concentration. Values of $K$ have been calculated by the use of equation (3) for those experiments in which the analytical error is not greater than two per cent and where the value of the uncomplexed organic reagent concentration calculated by difference is subject to small error.

The average value for the equilibrium quotient, using the best applicable experimental values, was 11·6 at 35°C, 9·1 at 25°C and 7·3 at 12·4°C. The trend toward lower values with decreasing temperature is apparent. An approximate value for $\Delta H$ of 1·3 kcal/mole was calculated from the slope obtained by plotting log $K$ versus $1/T$. The small value for $\Delta H$ is expected in view of the very slight effect of temperature on the equilibrium.

The ratio of the total concentration of acid to TOPO has been plotted in Fig. 2 against the equilibrium aqueous acidity. The limiting values of $(TOPO)_o/(HNO_3)_o$ are 1·10 at 12·4°C, 1·00 at 25°C and 0·88 at 35°C. The formation of a 1 : 1 adduct is strongly supported, but the limiting value of 0·88 at 35°C indicates the formation of species in which more than one mole of nitric is extracted per mole of reagent.

It is likely that the TOPO molecules at the aqueous–organic interface have the polar $\overset{-}{O}—\overset{+}{P}$ grouping directed toward the aqueous phase which is of high dielectric constant. The polar grouping may possibly extend across the interface and into the aqueous phase. The extraction of the nitric acid would probably involve bonding of the proton to the negative end of the $\overset{-}{O}—\overset{+}{P}$ dipole. The nitrate ion would be carried into the organic phase in order to maintain electrical neutrality. The scheme may be summarized as follows:

$$H_3O^+_{(a)} + NO^-_{3(a)} + \overset{-}{O}—\overset{+}{PR}_{3(o)} \rightleftharpoons H_2O - - - \overset{+}{H} - - - \overset{-}{O}—\overset{+}{PR}_3 + NO^-_{3(a)}$$

$$H_2O_{(a)} + (NO_3H \cdot OPR_3)_{(o)}.$$

The middle term suggests the nature of the equilibrium species at the interface.

The formation of the indicated complex should bring about a shift in the phosphoryl stretching frequency as a result of the interaction between the proton and the phosphoryl oxygen. DAASCH and SMITH[4] found the phosphoryl stretching frequency for trisubstituted phosphine oxides at 1176–1190 $cm^{-1}$. In the case of TOPO, this band has been found at 1194 $cm^{-1}$.[5] After saturation with nitric acid, the 1194 $cm^{-1}$ TOPO band is shifted to 1110 $cm^{-1}$. This represents an abnormally high shift when

[4] For a discussion of the work of DAASCH and SMITH, and other pertinent references, see L. J. BELLAMY, *The Infra-Red Spectra of Complex Molecules* p. 312. John Wiley, New York (1958).

[5] J. C. WHITE, *The Use of Tri-n-octylphosphine Oxide in Analytical Chemistry*. Special Technical Publication No. 238, ASTM (1958).

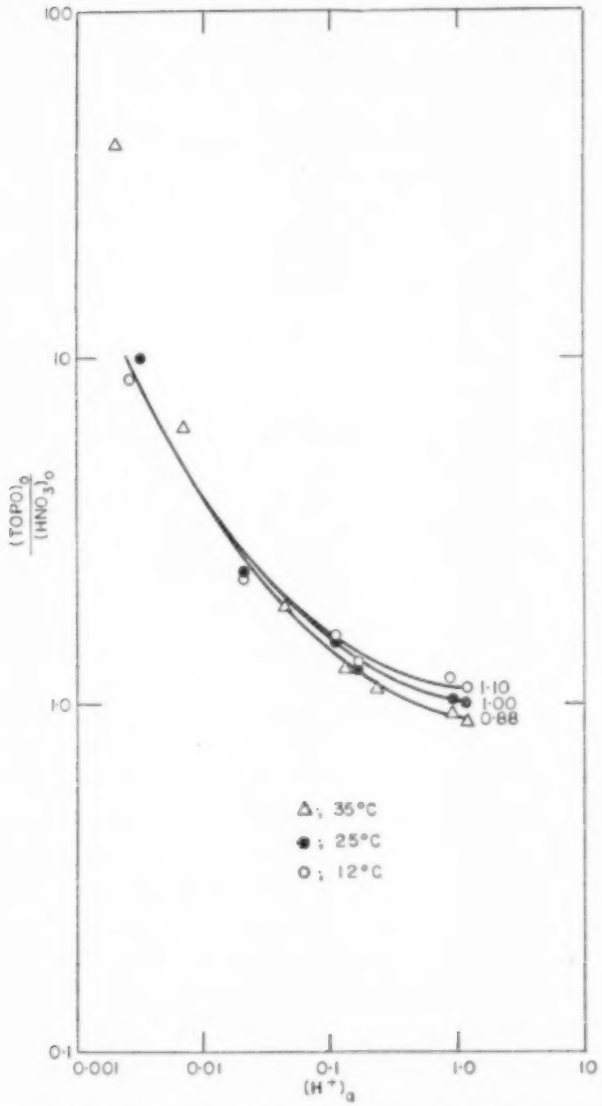



FIG. 2.—Ratio of organic reagent to nitric acid concentration in cyclohexane solution as a function of equilibrium aqueous acidity.

contrasted with the 10–20 $cm^{-1}$ change which is observed for hydrogen bonded carbonyl linkages. This shift of 84 $cm^{-1}$ is not unexpected, however, in view of the correspondingly high changes observed by DAASCH and SMITH in the case of hydrogen bonded phosphoryl groups of amino phosphorous compounds. In addition, BELLAMY and BEECHER[6] have shown that for silver salts of dialkyl phosphates the bands ascribed to the P=O vibration and P—OH deformation in the free acid disappear,

[6] L. J. BELLAMY and L. BEECHER, *J. Chem. Soc.* 1701 (1952).

and are replaced by a single band in the 1056–1110 $cm^{-1}$ region presumably attributed to an ionic phosphate group. These observations strongly suggest a structure approaching the type $(R_2\overset{+}{P}—OH)\overset{-}{NO_3}$ for the nitric acid–TOPO adduct.

*Extraction of thorium nitrate*

In Table 2 the data of Ross and WHITE[17] are given for the "loading" of cyclohexane–TOPO solutions by aqueous thorium nitrate in 1 M nitric acid.

TABLE 2.—COMPOSITION OF CYCLOHEXANE–TOPO SOLUTIONS AFTER EQUILIBRATION WITH NITRIC ACID–THORIUM NITRATE SOLUTIONS
Total thorium, 233 mg; acidity, 1 M; phase ratio, 1.

| TOPO, total | Thorium, total (mM) | Nitrate, total | $(TOPO)_o/(Th)_o$ | $(NO_3)_o/(Th)_o$ |
|---|---|---|---|---|
| 1·0 | 0·33 | | 3·0 | |
| 0·75 | 0·26 | | 2·9 | |
| 0·50 | 0·17 | | 2·9 | |
| 0·25 | 0·09 | | 2·8 | |
| 0·70 | 0·259 | 1·24 | 2·7 | 4·7 |
| 0·70 | 0·259 | 1·24 | 2·7 | 4·7 |
| 0·70 | 0·259 | 1·17 | 2·7 | 4·5 |
| 0·70 | 0·259 | 1·13 | 2·7 | 4·4 |

Vol. 12 59/60

These data show that a $(TOPO)_o/(thorium)_o$ ratio of about 3 : 1 exists in the thorium saturated organic phase. However, the ease of extraction of nitric acid and the relatively high acidity result in concurrent extraction of the acid. This is shown by the nitrate ion concentration in the organic phase which is in excess of that required for extraction of thorium alone, as the tetranitrate.

In Fig. 3 are shown the results obtained in the present investigation when the equilibrium aqueous thorium concentration was plotted against the equilibrium ratio $(TOPO)_o/(Th)_o$. The value of $(TOPO)_o$ represents the initial organic reagent concentration less the nitric acid concentration of the organic phase. The latter correction is made with the assumption that 1 mole of TOPO is associated with each mole of nitric acid extracted. The thorium ion concentration was varied from 0·00002 to 0·5 M while maintaining the initial acidity at 0·097 M. The latter value was as low as 0·07 M at equilibrium because the amount of acid extracted increased with decreasing concentration of thorium. At higher thorium concentrations, 0·03–0·05 M, the organic reagent is essentially completely combined with the acid and metal salt so that calculations of the frees, equilibrium concentration of TOPO were not made. At lower thorium concentrations, 0·01–0·002 M, the equilibrium concentration of thorium in the aqueous phase was so low, $10^{-6}$ M, that values of the extraction coefficient were subject to considerable analytical error. No attempt was made to calculate equilibrium quotients employing these values. However, the "loading" data clearly suggest a 3 : 1 molar ratio between the organic reagent and thorium nitrate in the organic phase. The thirteen values at the highest thorium concentrations have an average value of 3·07 with the minimum and maximum values being 2·71 and 3·11,

respectively, after correcting for extracted nitric acid. These results indicate the independence of the nitric acid–TOPO and thorium nitrate–TOPO equilibria, when both are present in the indicated range of concentration.

The simplest generalized equation for the extraction of thorium nitrate can be written as follows:

$$Th^{+4}{}_{(a)} + 4NO_3^- + n\text{TOPO} \rightleftharpoons Th(NO_3)_4 \cdot n\text{TOPO}. \quad (4)$$

If all concentrations are small relative to nitrate, i.e., the nitrate concentration is relatively unchanged before and after equilibrium, $n$ can be determined by a plot of log $D_a^o$ vs. log (TOPO), where $D_a^o$, the extraction coefficient is defined as follows:

$$D_a^o = \frac{\text{Thorium concentration in the organic phase}}{\text{Thorium concentration in the aqueous phase}}$$

and (TOPO) represents the free, uncomplexed, equilibrium concentration of the organic reagent. Among the simplifying assumptions made are that the organic

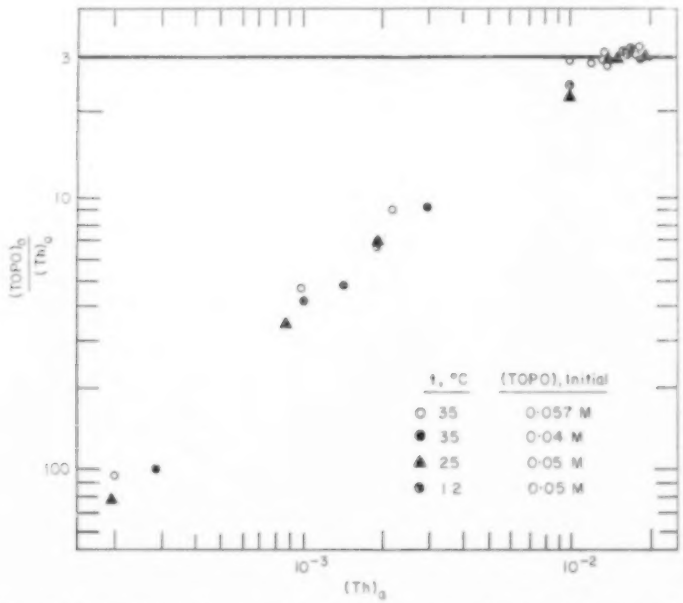



FIG. 3.—Ratio of organic reagent to thorium concentration in cyclohexane solution as a function of equilibrium aqueous thorium concentration.

reagent exists in the simple monomeric species in solution, that a single extracted species of complex is formed, and that the activity coefficients of the various species are essentially unchanged over the range of concentrations and conditions investigated.

A test of the dependency of the extraction on the TOPO concentration was made by varying the initial reagent concentration from 0·1 to 0·00025 M at constant initial aqueous concentrations of thorium and hydrogen ion. The acidity was maintained at a much lower level than that employed by ROSS and WHITE so as to minimize complications resulting from extraction of the acid. Assuming the formation of a

3 : 1 TOPO–thorium nitrate complex, from equation (4), the following relationship is obtained:

$$\log K = \log D_a^{\circ} - [4 \log (NO_3^-) + 3 \log (TOPO)].$$

If the formation of a 3 : 1 complex is correct, values of $K$ calculated on the basis of this assumption should be constant. Also, a plot of $\log D_a^{\circ}$ against log (TOPO) at constant nitrate ion concentration should have a slope of three.

Inasmuch as a direct measure of the free TOPO, or of the organic hydrogen ion concentration, was not available, both these values had to be calculated by difference. The equilibrium concentration of free TOPO, $(TOPO)_e$, was calculated as follows:

$$(TOPO)_e = (TOPO)_i - [3(Th)_o + (H^+)_o]$$

where $(TOPO)_i$ is the initial concentration of TOPO, and $(Th)_o$ and $(H^+)_o$ are equilibrium concentrations of thorium and hydrogen ion in the organic phase. The errors introduced by the use of values based on differences will be large in those cases where the TOPO is essentially all complexed, but should be small in the more concentrated reagent solutions.

Assuming the formation of the 3 : 1 complex and a constant nitrate ion concentration of 2 M, the following simplified form of the concentration equilibrium quotient results.

$$K = \frac{D_a^{\circ}}{16(TOPO)_e^3} \tag{5}$$

Listed in Table 3 are the data used to calculate $K$ according to equation (5). Values of $K$ were not calculated in those cases where $D_a^{\circ}$ was too indefinite due to the

TABLE 3.—THORIUM NITRATE EXTRACTION AS A FUNCTION OF VARIABLE TOPO CONCENTRATION
Initial aqueous thorium concentration, 0·00957 M; initial acidity, 0·00983 M
Initial aqueous thorium concentration, 0·01035 M at 12°C

| Temp. (°C) | $(Th)_a$ | $(Th)_o$ | $(Th)_b$* | $D_a^{\circ}$ | $(H^+)_a$ | $(H^+)_o$ | $(TOPO)_i$ (M) | $(TOPO)_e$ | $K$ |
|---|---|---|---|---|---|---|---|---|---|
| 25 | $<2 \times 10^{-6}$M | 0·0097 | — | $\sim 4 \times 10^3$ | 0·0060 | 0·0038 | 0·1 | 0·067 | |
| | $<2 \times 10^{-6}$ | 0·0095 | — | $\sim 4 \times 10^3$ | 0·0060 | 0·0038 | 0·05 | 0·018 | |
| | 0·00168 | 0·0077 | 0·00938 | 4·6 | 0·0067 | 0·0011 | 0·025 | | |
| | 0·00577 | 0·0037 | 0·00947 | 0·641 | 0·0095 | 0·0003 | 0·0125 | 0·0011 | $3 \times 10^7$ |
| | 0·00836 | 0·0014 | 0·00978 | 0·170 | 0·0095 | 0·0003 | 0·0050 | 0·00071 | $3 \times 10^7$ |
| | 0·00905 | 0·00071 | 0·00976 | 0·079 | 0·0098 | — | 0·00250 | 0·00037 | $9 \times 10^7$ |
| | 0·00948 | 0·000086 | 0·00957 | 0·0091 | 0·0097 | 0·0001 | 0·00050 | 0·00024 | $4 \times 10^7$ |
| | 0·00991 | 0·000038 | 0·00995 | 0·0038 | 0·0099 | — | 0·00025 | 0·00014 | $9 \times 10^7$ |
| 35 | $\sim 10^{-6}$ | 0·0101 | | $\sim 10^3$ | 0·0069 | 0·0029 | 0·1 | 0·065 | |
| | $\sim 10^{-6}$ | 0·0099 | | $\sim 10^3$ | 0·0091 | 0·0007 | 0·05 | 0·020 | |
| | 0·0026 | 0·00698 | 0·00958 | 2·69 | 0·0091 | 0·0007 | 0·025 | 0·003 | |
| | 0·0059 | 0·00392 | 0·00982 | 0·664 | 0·0098 | — | 0·0125 | 0·00074 | $1 \times 10^8$ |
| | 0·0084 | 0·00130 | 0·00970 | 0·154 | 0·0091 | 0·0007 | 0·0050 | 0·00040 | $1 \times 10^8$ |
| | 0·0095 | 0·00016 | 0·00966 | 0·017 | 0·0098 | — | 0·00050 | 0·00002 | $1 \times 10^9$ |
| | 0·0095 | 0·000073 | 0·00957 | 0·0077 | 0·0096 | 0·0002 | 0·00025 | — | |
| 12 | $\sim 10^{-6}$ | 0·01034 | | $\sim 10^3$ | 0·0054 | 0·0044 | 0·1 | 0·065 | |
| | $\sim 10^{-6}$ | 0·00991 | | $\sim 10^3$ | 0·0077 | 0·0021 | 0·05 | 0·018 | |
| | 0·0024 | 0·00762 | 0·01002 | 3·2 | 0·0087 | 0·0011 | 0·0250 | 0·001 | $2 \times 10^6$ |
| | 0·00625 | 0·00409 | 0·01034 | 0·654 | 0·0094 | 0·0004 | 0·0125 | — | |
| | 0·00875 | 0·00151 | 0·01026 | 0·173 | 0·0099 | | 0·0050 | 0·00047 | $1 \times 10^8$ |
| | 0·00961 | 0·000711 | 0·01032 | 0·0740 | 0·0096 | 0·0002 | 0·0025 | 0·00017 | $5 \times 10^7$ |
| | 0·01034 | 0·000121 | 0·01046 | 0·00117 | 0·0096 | 0·0002 | 0·0005 | — | |

* $(Th)_b$ = Thorium balance; total thorium concentration in both phases by analysis.

extremely dilute aqueous thorium levels at high organic reagent concentrations. In addition, $K$ values could not be calculated when the analyses showed that the concentrations of the extracted species equalled or exceeded the reagent concentration.

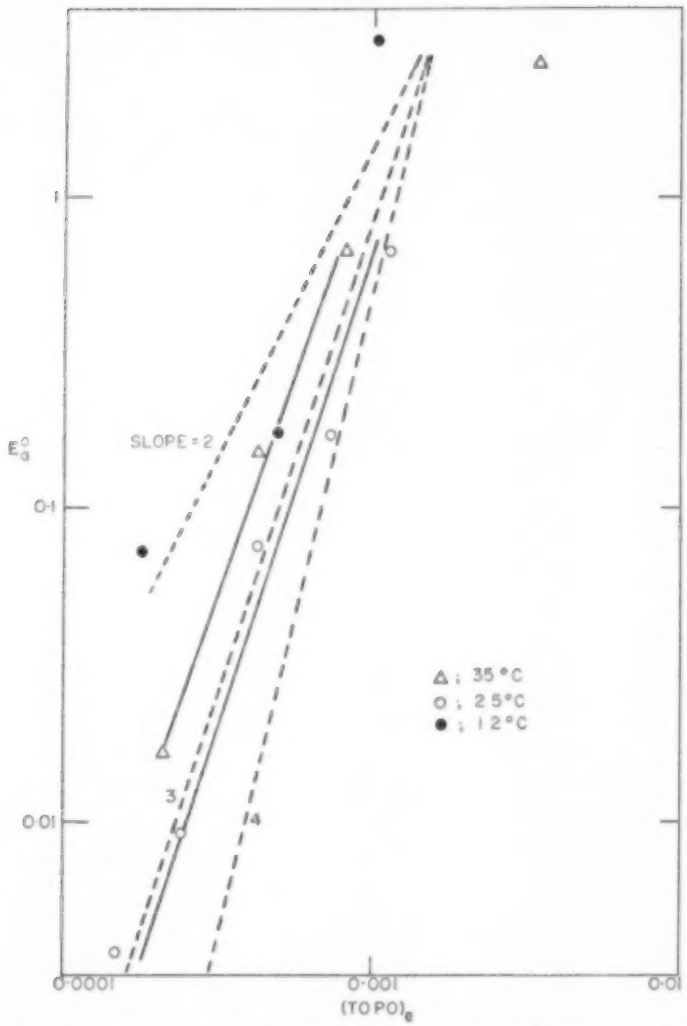



FIG. 4.—Distribution of thorium nitrate between water and cyclohexane as a function of equilibrium TOPO concentration.

Where the data permitted calculation of $K$ values, the general agreement is quite satisfactory. It is to be noted that there is no apparent trend in the equilibrium quotient at the different temperatures investigated. This indicates that the temperature effect is very slight, or that the experimental procedure used is not sufficiently sensitive for the purpose of measuring the change in $K$ with temperature.

In Fig. 4 those values of $D_a^\circ$ and $(TOPO)_e$, for which $K$ values have been determined, have been plotted on logarithmic axes. Dashed lines of slopes two, three and four have been drawn and it is noted that the solid lines for the 25°C and 35°C points best fit a slope of three. The 12°C points are too scattered to be indicative. The results at 25°C and 35°C support the proposed formation of a 1 : 3 thorium nitrate–TOPO adduct.

Vol. 12 1959/6

Results obtained at higher acidities and at a higher constant concentration of thorium nitrate are shown in Table 4. The purpose of these experiments was to obtain more accurate analytical values so that temperature effects might be more critically observed. While the thorium material balance is very good, indicating reliable analytical values, it is to be noted that it was not possible in every experiment to calculate the value of $(TOPO)_e$. In the latter cases, the respective concentrations of acid and thorium in the organic phase were such that the assumption of a 1 : 1 and 1 : 3 complex required TOPO concentrations in excess of that initially present. Although the values at 25°C were such that a finite equilibrium concentration of TOPO was calculated in almost every case, a log–log plot yielded a completely scattered set of points. It is clear that at higher acidities, $[(H^+) \geqslant 0{\cdot}08\ M]$, the equilibrium reaction given in equation (4) is inadequate.

TABLE 4.—THORIUM NITRATE EXTRACTION BY TOPO AT HIGHER ACIDITIES
Initial concentration of Th = 0·0207
Initial concentration of TOPO = 0·05

| Temp. (°C) | $(Th)_a$ | $(Th)_o$ | Material balance | $(H^+)_i$ | $(H^+)_a$ | $(H^+)_o$ | $E_a°$ | $(TOPO)_e$ |
|---|---|---|---|---|---|---|---|---|
| 12 | 0·00625 | 0·0134 | 0·0197 | 1·92 | 1·83 | 0·09 | 2·14 | * |
| | 0·00664 | 0·0138 | 0·0204 | 1·33 | 1·36 | — | 2·08 | 0·0086 |
| | 0·00638 | 0·0142 | 0·0206 | 1·15 | 1·12 | 0·029 | 2·23 | * |
| | 0·00513 | 0·0146 | 0·0197 | 0·77 | 0·69 | 0·076 | 2·85 | * |
| | 0·00513 | 0·0151 | 0·0202 | 0·38 | 0·38 | 0·003 | 2·94 | 0·0017 |
| | 0·00418 | 0·0155 | 0·0197 | 0·23 | 0·23 | — | 3·71 | 0·003 |
| | 0·00444 | 0·0164 | 0·0208 | 0·077 | 0·073 | 0·003 | 3·69 | * |
| 25 | 0·00797 | 0·0125 | 0·0205 | 1·92 | 1·93 | — | 1·57 | 0·0125 |
| | 0·00741 | 0·0129 | 0·0203 | 1·33 | 1·33 | — | 1·74 | 0·0113 |
| | 0·00703 | 0·0134 | 0·0204 | 1·15 | 1·16 | — | 1·91 | 0·010 |
| | 0·00612 | 0·0142 | 0·0203 | 0·77 | 0·76 | 0·006 | 2·32 | 0·0014 |
| | 0·00543 | 0·0155 | 0·0209 | 0·38 | 0·38 | 0·003 | 2·84 | 0·0005 |
| | 0·00483 | 0·0155 | 0·0203 | 0·23 | 0·23 | — | 3·21 | 0·0035 |
| | 0·00448 | 0·0160 | 0·0205 | 0·077 | 0·074 | 0·003 | 3·57 | * |
| 35 | 0·00819 | 0·0124 | 0·0206 | 1·92 | 1·88 | 0·04 | 1·51 | * |
| | 0·00776 | 0·0129 | 0·0207 | 1·33 | 1·34 | — | 1·67 | 0·0113 |
| | 0·00707 | 0·0142 | 0·0212 | 1·15 | 1·16 | — | 2·01 | 0·0074 |
| | 0·00633 | 0·0151 | 0·0214 | 0·77 | 0·77 | 0·006 | 2·38 | * |
| | 0·00534 | 0·0155 | 0·0208 | 0·38 | 0·38 | 0·003 | 2·90 | 0·0005 |
| | 0·00483 | 0·0159 | 0·0207 | 0·23 | 0·22 | 0·01 | 3·29 | * |
| | 0·00452 | 0·0164 | 0·0209 | 0·077 | 0·072 | 0·05 | 3·62 | * |

* $3(Th)_o + (H^+)_o > (TOPO)_e$

At higher acidities, the extraction of acid by the organic reagent is appreciable and the thorium extraction is no longer independent of the acid extraction. The $TOPO{\cdot}HNO_3$ complex may itself act as the extracting agent leading to adducts of the type $Th(NO_3)_4{\cdot}nHNO_3{\cdot}3TOPO$. An alternative mechanism leading to the same end would involve the formation, at higher acidity and high nitrate ion concentration, of $H_2Th(NO_3)_6$ in the aqueous phase and the direct extraction of this species. The

formation of thorium complexes of coordination number of six is well known.

In conclusion, it may be said that the effect of temperature, in the range of concentrations reported and in the temperature range investigated, is extremely small and is of little effect in enhancing or suppressing the extraction of thorium from an analytical, or hydro-metallurgical point of view. This suggests that the heat of transfer of thorium nitrate from the aqueous into the TOPO–cyclohexane solution is very small. This small heat of transfer may result from the fact that the heat of hydration of thorium nitrate and the heat of formation of the thorium nitrate–TOPO complex are of about the same order of magnitude.

The formation of a $Th(NO_3)_4 \cdot 3TOPO$ complex seems to be fairly well established provided that the aqueous phase is fairly dilute with respect to both thorium and acidity (maximum concentration of each, 0·01 M). At higher concentrations and acidities other species are involved.

A quantitative understanding of this problem will require alternative experimental techniques. The most obvious approach is the use of very dilute solutions that contain tracer thorium. This will make possible more accurate determinations of the residual thorium concentrations under conditions where the extraction coefficient is very high. Also, this will make possible the use of very dilute solutions so that the organic reagent concentration will not be effectively changed after equilibrium and its concentration also can be calculated with considerably greater accuracy.

Work carried out under Contract No. W–7405–eng–26 at Oak Ridge National Laboratory, operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

Vol.
12
1959/6

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 327 to 335. Pergamon Press Ltd. Printed in Northern Ireland

# THE EXTRACTION OF ACTINIDE ELEMENTS FROM NITRIC ACID SOLUTIONS BY TRI-n-OCTYLAMINE*

W. E. KEDER, J. C. SHEPPARD† and A. S. WILSON
Hanford Laboratories Operation, General Electric Company,
Richland, Washington

(*Received* 25 *May* 1959)

**Abstract**—The extraction of six of the actinide elements from nitric acid solutions by tri-n-octylamine in xylene has been investigated and the effects of acid and amine concentrations have been measured. The extraction of neptunium(IV) and plutonium(IV) was found to be much greater than any of the other oxidation states studied. The application of this property to a separation technique has been suggested. The nitrate complex species predominating in the amine phase has been suggested in the case of the tetravalent ions.

LONG chain tertiary amine salts are soluble in a variety of organic solvents which are immiscible with aqueous solutions. This property of long chain tertiary amines permits extraction of acids and metallic anions from acidic solutions. SMITH and PAGE[1] have extracted a variety of weak and strong acids from aqueous solutions with a chloroform solution of methyldioctylamine. MOORE has used tri-iso-octylamine to extract plutonium(VI) from hydrochloric acid solutions.[2] A principal use of these high molecular weight amines has been to extract uranium from sulphuric[3,4,5] and hydrochloric[6] acid solutions. A high molecular weight quaternary amine has been used in extracting plutonium(IV) from nitric acid solutions.[7] Moreover, an amine mixture has been used in the investigation of plutonium(IV) nitrate complexes in aqueous solutions.[8] Trilaurylamine has been suggested as an extraction agent to remove plutonium from nitric acid solutions of irradiated uranium.[9] The present paper describes the extraction behaviour of the actinide elements: thorium, protactinium, uranium, neptunium, plutonium and americium from nitric acid solutions using a xylene solution of tri-n-octylamine as the extraction agent. Of the oxidation states investigated, only plutonium(IV) and neptunium(IV) were found to extract appreciably.

## EXPERIMENTAL PROCEDURE

### A. *Chemicals*

Tri-n-octylamine (TOA) obtained from the Chemical Procurement Company, 550 Fifth Avenue, New York 36, New York, was used without further purification. An acid equivalence determination

* Presented before the Northwest Regional Meeting of the American Chemical Society, Portland, Oregon, June, 1958.

† Present address: Department of Chemistry, San Diego State College, San Diego, California.

[1] E. L. SMITH and J. E. PAGE, *J. Soc. Chem. Ind.* **67**, 48 (1948).
[2] F. L. MOORE, *Analyt. Chem.* **30**, 908 (1958).
[3] K. B. BROWN *et al.*, Report AECD-4142 (1954).
[4] C. F. COLEMAN *et al.*, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, P/510, Vol. 28, p. 278. United Nations (1959).
[5] K. G. ALLEN, *J. Amer. Chem. Soc.* **80**, 4133 (1958).
[6] R. H. BAILES, *Progress Report* DOW-157 (1957).
[7] B. GOLDSCHMIDT *et al.*, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, P/349, Vol. 9, p. 492. United Nations (1956).
[8] J. A. BROTHERS *et al.*, *J. Inorg. Nucl. Chem.* **7**, 85 (1958).
[9] A. S. WILSON, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, P/544, Vol. 17, p. 348. United Nations (1959).

yielded a value of 375 g/mole of hydrogen ion. The theoretical value is 354. The amine was light yellow in colour, and its nitrate salt was pink to brown in colour in xylene. Xylene was Baker's reagent grade; it was used without further purification. Ferrous sulphamate was prepared by dissolving iron filings in a solution of sulphamic acid at about 80–90 C. The solution was stirred by nitrogen aeration which also served to prevent oxidation of the ferrous ion formed. The solution was filtered before using. Other chemicals were of reagent grade. Laboratory distilled water was used.

B. *Extraction procedure*

All extractions were conducted at room temperature (25 C). Ten volume per cent (10 v/o) tri-n-octylamine in xylene was stirred with equal volumes of nitric acid solution of the desired composition for 3–5 min. Phase equilibrium was reached in about 1 min in all cases tested. Phases were separated by centrifugation after contacting. Suitable aliquots were taken for analyses.

C. *Source and analyses of the actinide elements*

1. *Thorium.* Thorium-234 tracer for these experiments was separated from a nitric acid solution of the actinide elements by an ion exchange procedure. Radiochemical purity was established by $\gamma$-spectrum analysis; however, an unknown quantity of other thorium isotopes was thought to be present. As in the case of all the isotopes used here, active impurities were below detection of the instruments used, i.e. less than one per cent.

No oxidation state adjustment was required to obtain thorium(IV). Thorium was determined by $\gamma$-counting in a scintillation well counter. Sufficient time was allowed to elapse between the separation of phases and counting for secular equilibrium to be established with protactinium-234.

2. *Protactinium.* Daughter protactinium-233 was separated from a nitric acid stock solution of neptunium-237 by anion exchange. Measurement of purity and counting of this isotope were by the same techniques as for thorium-234. No valence adjustment was needed to maintain protactinium(V).

3. *Uranium.* Uranium(VI) was obtained as uranyl nitrate hexahydrate. Solutions of the proper concentrations were prepared and contacted in the usual manner. Uranium(VI) analyses were conducted in several ways;[10] Jones reductor–ceric sulphate titration, X-ray photometer and fluorometric methods. Uranium tracer as uranium-233 was used in some experiments. The uranium-233 tracer was obtained as uranyl nitrate in a nitric acid solution. An $\alpha$-energy analysis indicated that the tracer was at least 99 per cent uranium-233. Uranium-233 was counted by direct mounting.

Uranium(IV) nitrate solutions were prepared by the metathesis of uranium(IV) fluoride with hot 6 M sodium hydroxide. The hydrous uranium(IV) oxide was washed several times with 0·1 M sodium hydroxide. The hydrous oxide was dissolved in cool nitric acid containing 0·1 M urea to give green solutions of uranium(IV). The urea was added as a suppressor for the nitrite ion catalysed reaction between nitrate ion and uranium(IV) ion. Uranium(IV) ion was measured by adding an aliquot of the solution of interest to a measured excess of standard ceric ion. The excess ceric ion was titrated with standard ferrous ion using ferroin as an indicator. In these experiments, both total uranium and uranium(IV) were measured in the aqueous phase. Only total uranium was measured directly in the organic phase. An indirect measurement of uranium(IV) in the organic phase was made by stripping the organic phase with 1·0 M hydrofluoric acid solution and measuring the uranium(IV) in the resulting aqueous phase or strip solution.

4. *Neptunium.* Neptunium-239 tracer was prepared by tributyl phosphate extraction of neptunium(IV) from nitric acid solutions of freshly irradiated uranium-238. Radiochemical purity of the tracer was established by $\gamma$-spectrum analysis. Neptunium-237 was purified by anion exchange and its purity was measured by $\alpha$-energy analysis.

Neptunium(IV) distributions were done in the presence of ferrous sulphamate as a holding reductant, and neptunium(VI) distributions in the presence of sodium bromate as a holding oxidant. Neptunium(V) tracer was prepared by allowing neptunium(IV) to be oxidized ten days by 2 M nitric acid or by oxidizing to neptunium(VI) with permanganate and reduction to neptunium(V) with nitrous acid. Neptunium(V) distributions were made without holding oxidant or reductant.

Neptunium-237 was counted by direct plating. Analyses of neptunium-239 solutions were done by $\gamma$-counting in a scintillation well counter.

[10] C. J. RODDEN, *Analytical Chemistry of the Manhattan Project*, NNES, Plutonium Project Record, Vol. 8, p. 1. McGraw-Hill, New York (1950).

Vol. 12 1959/6

5. *Plutonium.* Plutonium was obtained in a nitric acid solution. Suitably sized aliquots of this solution were mixed with a nitric acid solution of the desired concentration. In some cases, where the plutonium extraction coefficients were large, the extraction coefficient was determined by back extracting the plutonium from the organic phase into a fresh aqueous phase. In this manner, non-extractable α-active elements, such as americium, did not interefere with the measured extraction coefficient.

Plutonium(VI) was prepared by oxidizing plutonium(IV) with 0·01 M ceric nitrate. During extraction, 0·05 M sodium bromate was used as the holding oxidant. Plutonium(IV) was kept in the four state by the use of 0·03–0·05 M sodium nitrite. Plutonium(III) was maintained with 0·05 M ferrous sulphamate and 0·01 M sulphamic acid was used as a nitrite ion suppressor. This method apparently maintained a high plutonium(III)/(IV) because successive extractions of the 1 and 6 M nitric acid solutions corroborated the distributions ratios listed in Table 1. All plutonium analyses were conducted by direct mounting and α-counting.

6. *Americium.* Americium-241 of suitable radiochemical purity as determined by α-energy analysis was obtained in a nitric acid solution. Analyses were conducted by α-counting.

## RESULTS AND DISCUSSION

The results of extraction experiments in which the distribution ratios into 10 v/o TOA–xylene were measured as a function of nitric acid concentration are presented in Table 1. The acid dependence of D* shows the same general features in most cases.

TABLE 1.—DISTRIBUTION RATIOS FOR EXTRACTION OF ACTINIDES FROM NITRIC ACID WITH 10 V/O TRI-n-OCTYLAMINE

| Molarity of $HNO_3$ | Th(IV) | Pa(V) | U(IV) | U(VI) | Np(IV) | Np(V) × $10^2$ | Np(VI) | Pu(III) | Pu(IV) | Pu(VI) | Am(III) × $10^4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1·0 | 0·24 | 0·20 | — | 0·2 | — | 3·6 | 2·0 | 0·006 | 140 | 0·9 | 3·6 |
| 2·0 | 0·48 | 0·28(0·45)* | 0·6–1 | 0·50 | 45 | 9·8 | 2·8 | 0·032 | 210 | 1·7 | 6·3 |
| 3·0 | — | 0·38 | — | 0·69 | — | 6·7 | 3·5 | 0·038 | 210 | — | 4·4 |
| 4·0 | 0·53 | 0·38 | — | 0·99 | 66 | 15 | 5·0 | 0·077 | 250 | 3·8 | 4·5 |
| 5·0 | — | 0·52 | — | 0·95 | 60 | — | 4·7 | 0·060 | 190 | — | — |
| 6·0 | 0·66 | 0·57 | — | 1·17 | 58 | 29 | 5·3 | 0·092 | 260 | 4·9 | 4·5 |
| 7·0 | — | 0·65 | — | 1·2 | 55 | — | — | 0·095 | 100 | — | — |
| 8·0 | 0·39 | 0·47 | — | 0·78 | 37 | 48 | 4·6 | 0·062 | 80 | 5·0 | 25 |
| 9·0 | — | 0·44 | — | 0·83 | 28 | — | — | — | 31 | — | — |
| 10·0 | 0·33 | 0·45 | — | 0·63 | 14 | 55 | 2·4 | — | 22 | 4·2 | 10 |
| 11·0 | — | — | — | 0·40 | — | — | — | — | 8 | — | — |
| 12·0 | — | — | — | 0·26 | — | — | — | — | 4 | 1·7 | 14 |
| 14·0 | — | — | — | — | — | — | — | — | — | 0·9 | — |

* From Table 2.

There is a general rise in $D$ with increase of acid concentration, a maximum at about six molar acid, and a decrease in $D$ to the highest concentrations measured. Distribution ratio for the oxidation states studied vary over a range of six orders of magnitude.

The species formed upon equilibration of an amine solution with nitric acid is thought to be $Octyl_3NH^+NO_3^-$. Equilibrium of this salt with metal ion solution then extracts a metal anion which replaces the nitrate ion. The resulting ion pair must be uncharged so that the number of amine cations required equals the negative charge of the metal anion. The slope of a log–log plot of $D$ vs. TOA concentration is a measure of the amine-to-anion ratio and, hence, of the anion charge. It should be noted that this is the extracted anion species and is not necessarily the same anion which predominates in the aqueous phase. Distribution ratios for the extraction of the actinide

* Distribution ratio $D$ is the ratio of concentration in the organic phase to concentration in the aqueous phase.

TABLE 2.—DISTRIBUTION RATIOS FOR EXTRACTION OF ACTINIDES FROM 4 M NITRIC ACID AS A FUNCTION OF AMINE CONCENTRATION

| Vol. per cent TOA in xylene | Th(IV) | Pa(V)* | Pa(V) | U(VI) | Np(IV)† | Np(IV) | Np(VI) | Pu(III) | Pu(IV)* | Pu(VI) | Am(III) × $10^4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0·1 | 0·0013 | 0·00010 | 0·00026 | 0·0018 | — | 0·012 | 0·0094 | — | 0·18 | — | — |
| 0·5 | 0·010 | — | 0·0035 | 0·018‡ | 0·14 | 0·12 | 0·083 | 0·00055 | 0·64 | 0·081 | — |
| 1·0 | 0·041 | 0·0058 | 0·013 | 0·066‡ | 0·58 | 0·43 | 0·187 | 0·00028 | 2·20 | 0·24 | — |
| 2·0 | 0·168 | — | 0·039 | 0·10 | 2·3 | 1·74 | 0·66 | 0·0027 | 9·4 | 0·42 | 1·6 |
| 3·0 | — | — | — | 0·21 | 5·10 | — | — | — | 18·4 | — | — |
| 4·0 | 0·66 | — | — | 0·47 | — | — | 1·88 | 0·007 | — | 1·06 | 1·8 |
| 5·0 | — | 0·075 | 0·16 | 0·50 | 11·8 | 14 | — | — | 78 | — | — |
| 7·0 | 1·53 | — | — | 0·69 | — | — | 3·94 | 0·025 | — | 2·26 | 1·9 |
| 8·0 | — | — | — | — | 30 | — | — | — | — | — | — |
| 10·0 | 2·88 | 0·18 | 0·45 | 1·22‡ | 37 | 53 | 5·32 | 0·048 | $2·5 \times 10^2$ | 3·68 | 5·6 |
| 20·0 | 10·2 | 0·37 | 1·87 | 2·72‡ | 106 | 175 | 15·4 | 0·080 | $8·5 \times 10^2$ | 9·5 | 7·6 |
| 30·0 | 21·7 | — | 2·5 | 4·42‡ | — | 306 | 19·6 | 0·23 | — | 16·0 | 12·0 |
| 50·0 | — | 1·62 | 3·5 | — | 284 | — | — | — | $1·39 \times 10^3$ | — | — |
| 100·0 | — | 2·36 | — | — | 720 | — | — | — | $2·71 \times 10^3$ | — | — |

* 2 M $HNO_3$ solutions.
† 8 M $HNO_3$ solutions.
‡ Average of $U_{233}$ extraction results and natural uranium extraction results determined by X-ray photometry and fluorimetry

elements as a function of TOA concentration are given in Table 2. Slopes of log–log plots of these data have been determined and are discussed below.

A. *Tetrapositive oxidation states*

The results for the tetrapositive oxidation states are plotted in Fig. 1 and 2. Neptunium(IV) and plutonium(IV) are the most readily extractable of all the oxidation

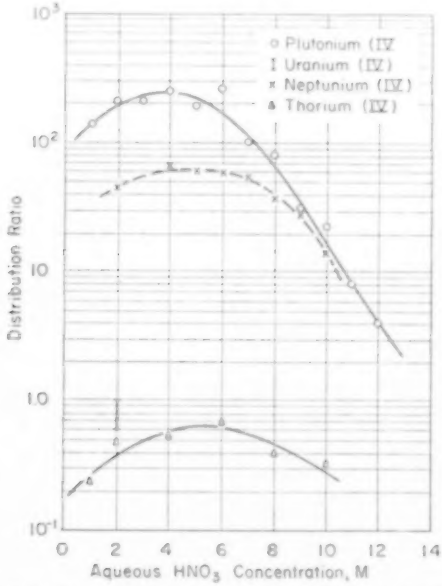



FIG. 1.—The extraction of the quadravalent actinide nitrates by 10 v/o TOA in xylene.

states studied. Thorium(IV) and uranium(IV) are much less extractable. This behaviour is parallel to a great extent to the extraction of these elements by tributyl phosphate (TBP). The distribution ratios into the amine are, however, about an order of magnitude above those obtained with 19 v/o TBP in a similar environment.[11,12]

[11] G. B. BEST *et al.*, *J. Inorg. Nucl. Chem.* **4**, 315 (1958).
[12] K. ALCOCK *et al.*, *J. Inorg. Nucl. Chem.* **6**, 328 (1958).

Vol. 12 1959/6

The high extractability of neptunium(IV) and plutonium(IV) is thought to be related to their tendency to form anionic complexes.

Log $D$ vs. log (v/o TOA) plots are shown in Fig. 2 for tetrapositive thorium, neptunium and plutonium. The resulting curves have slopes very nearly two at the lower amine concentrations. This indicates that the metal ion extracts with two amine cations. The data are, therefore, consistent with those expected of an extracted hexanitrato anion.

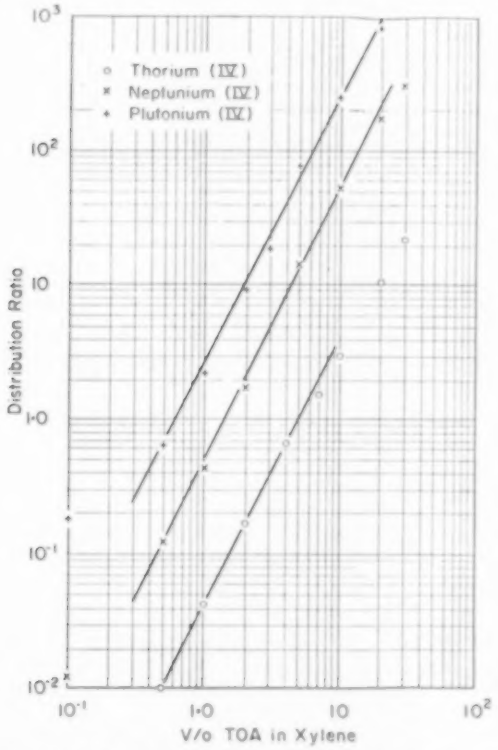



FIG. 2.—The extraction of thorium(IV) and neptunium(IV) nitrates from 4 M nitric acid and of plutonium(IV) from 2 M nitric acid.

The distribution ratio for uranium(IV) was measured only at two molar nitric acid. Higher acid concentrations were not used because of the increasing difficulty in preventing the oxidation of uranium(IV) to uranium(VI) by the nitric acid. In two molar nitric acid, the distribution ratio for uranium(IV) lies between 0·6 and 1·0. Table 3 lists the data from which these distribution ratios were obtained. The $D$ value, 0·6, was obtained by dividing the concentration of uranium(IV) found in the strip solution by the concentration of uranium(IV) found in the extracted aqueous solution. This value represents the lower limit of the distribution ratio. The upper limit, 1·0, of the distribution ratio was obtained by difference. The difference in uranium(IV) concentration between the initial aqueous solution and the extracted aqueous solution represents the maximum amount of uranium(IV) ion that could have

TABLE 3.—EXTRACTION OF U(IV) BY TRI-n-OCTYLAMINE
Aqueous: 2 M $HNO_3$, 0·1 M urea
Organic: 10 v/o TOA–xylene
Aqueous strip: 1 M HF
Equal volumes of phases used throughout.

| Solution | Concentration, g/l. | | Distribution ratio | |
|---|---|---|---|---|
| | U(IV) | U total | U(IV) | U total |
| Initial aqueous | 2·6 | 2·9 | — | — |
| Extracted aqueous | 1·3 | 1·8 | 1·0 | — |
| Organic | — | 1·3 | — | 0·72 |
| Aqueous strip | 0·8 | 1·1 | 0·61 | — |
| Stripped organic | — | 0·2 | — | — |

extracted. This value, 1·3 g/l., was divided by the amount of uranium(IV) remaining, 1·3 g/l., to give the upper limit of *D*.

B. *Hexapositive oxidation states*

The extraction data for uranium(VI), neptunium(VI) and plutonium(VI) are plotted in Figs. 3 and 4. Distribution ratios of neptunium(VI) and plutonium(VI) are

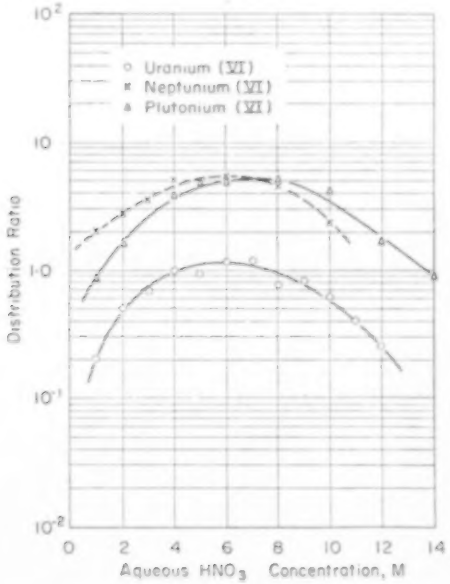



FIG. 3.—The extraction of the hexavalent actinide nitrates by 10 v/o TOA in xylene.

very close and are ten to one hundred times less than the *D* for the tetra-positive oxidation states of those elements. Extraction of uranium(VI) is lower still which permits an easy separation of neptunium(IV) and/or plutonium(IV) from uranyl nitrate solutions.

Vol. 12 1959/6

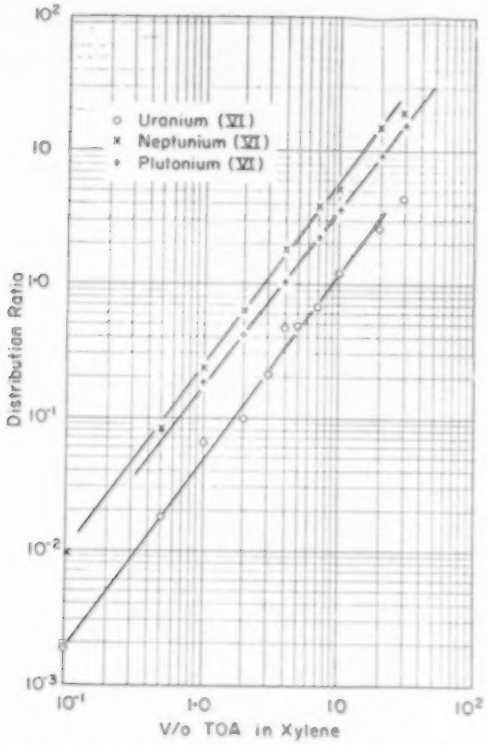



FIG. 4.—The extraction of the hexavalent actinide nitrates from 4 M nitric acid.

Slopes of the log $D$ vs. log (v/o TOA) plots in these cases are less than two but greater than unity.

C. *Tripositive and pentapositive oxidation states*

The extraction data obtained for protactinium(V), neptunium(V), plutonium(III) and americium(III) as a function of nitric acid concentration are plotted in Fig. 5. $D$ is seen to vary in the order Pa(V) > Pu(III) > Np(V) > Am(III). The general shapes of the curves are similar to those of the tetrapositive and hexapositive oxidation states.

Distribution ratios for these oxidation states, with the exception of neptunium(V), have been measured as a function of amine concentration and the results are plotted on a log–log scale in Fig. 6. The slopes of the curves for plutonium(III) and protactinium(V) are about one and one half. At the higher amine concentrations the slopes decrease somewhat. Americium(III) shows a slope of unity at the concentrations at which measurements were made.

HARDY *et al.*[13] have measured $D$ for protactinium(V) at 20°C as a function of nitric acid concentration at 0·1 and 0·5 M TOA in benzene and as a function of TOA concentration at 6 M $HNO_3$. We have interpolated their data to 10 v/o TOA and have plotted the results in Fig. 5 for comparison with our experimental data. Our

[13] C. J. HARDY, D. SCARGILL and J. M. FLETCHER, *J. Inorg. Nucl. Chem.* 7, 257 (1958).

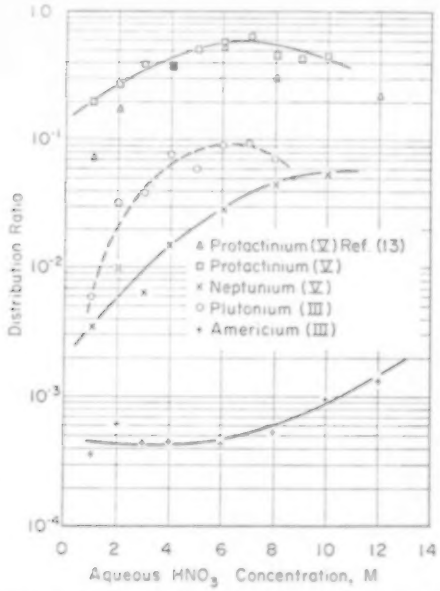



FIG. 5.—The extraction of pentavalent and trivalent actinide nitrates by 10 v/o TOA in xylene.

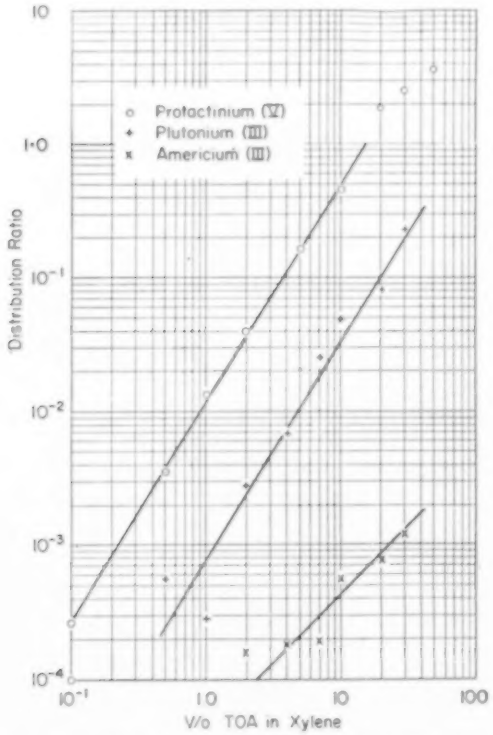



FIG. 6.—The extraction of protactinium(V), plutonium(III) and americium(III) from 4 M nitric acid.

Vol. 12 1959/6

data show higher distribution ratios at low acid and high acid but agreement is good at the intermediate acid concentrations. These authors obtain a slope of unity from a plot of log $D$ vs. log amine concentration. From this they conclude that the charge on the protactinium anion is $-1$; which, of course, must be only the extracted anion. Our slope for the 4 M $HNO_3$ solutions is about 1·5. In 2 M $HNO_3$, however, the slope at high amine concentrations is approximately unity. (See Table 2.)

D. *Application to separation techniques*

The high distribution ratios found for neptunium(IV) and plutonium(IV) and the lower distribution ratios found for the other actinide elements show that neptunium and plutonium can be readily separated from nitric acid solutions of the actinide elements. WILSON[9] has reported the use of the tertiary amine, trilaurylamine, as an extraction agent for the removal of plutonium from nitric acid solutions of irradiated uranium and has discussed the decontamination of plutonium from fission products. By proper selection of acidity and oxidation environment, it is possible to extract plutonium and neptunium individually or simultaneously. In the latter case advantage may be taken of the relatively slow oxidation of neptunium(IV) to neptunium(V) under conditions where plutonium(IV) is stable. Such conditions are obtained in approximately 8 molar nitric acid with 0·10 molar sodium nitrite. It is also obvious from the distribution data that very good separation of neptunium from plutonium is possible. The plutonium can be held in the three state while the neptunium(IV) is extracted into the organic phase. Plutonium and/or neptunium should be easily separated from the higher members of the actinide group, since these elements may be expected to behave much like americium.

Such applications as the removal of daughter protactinium from neptunium-237 and the separation of thorium from neptunium and/or plutonium also suggest themselves.

*Acknowledgements*—We wish to express our appreciation to Mrs. L. P. POWER who conducted most of the distribution experiments.

Most of the chemical and radiochemical analyses were performed by the personnel of the Analytical Laboratories, Mr. E. W. CHRISTOPHERSON, Manager.

The work was performed under Contract No. AT(45-1)-1350 for the U.S. Atomic Energy Commission.

Vol. 12 59/60

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 336 to 342. Pergamon Press Ltd. Printed in Northern Ireland

# SOLVENT EXTRACTION OF SCANDIUM, YTTRIUM AND LANTHANUM BY THE MONOALKYL ORTHOPHOSPHORIC ACIDS

C. G. WARREN* and J. F. SUTTLE†
University of New Mexico, ‡ Albuquerque, New Mexico

(*Received* 17 *March* 1959)

**Abstract**—The extraction of scandium(III), yttrium(III) and lanthanum(III) into an amyl alcohol solution containing the mono(n-alkyl) orthophosphoric acid, $H_2RPO_4$, from an aqueous $HNO_3$ solution was investigated. The variation of the distribution of these elements with the concentration of both $HNO_3$ and $H_2RPO_4$ indicated that the complexes, tentatively identified as $Sc(HRPO_4)_3$, $HY(HRPO_4)_4$, and $HLa(HRPO_4)_4$, were extracted.

The mono(n-alkyl) orthophosphoric acids were synthesized by first preparing the alkyl dichloro phosphate from the normal alcohol and phosphorus (V) oxychloride. This was hydrolysed to the corresponding $H_2RPO_4$.

NUMEROUS papers have appeared in the current literature describing the liquid–liquid extraction of metal ions through complex formation with one of the organic esters of orthophosphoric acid. The butyl derivatives, for example, have been extensively studied and adapted to the separation of many metal ions by solvent extraction techniques.[1] The octyl phosphoric acids have been used in separations of the lanthanide and actinide elements.[2,3,4] The higher alkyl phosphoric acid esters have been employed to extract uranium from its ore.[5,6]

The work reported here was restricted to various mono(n-alkyl) orthophosphoric acids, symbolized as $H_2RPO_4$.§ These primary esters were used to study the reaction occurring in the liquid–liquid extraction of scandium, yttrium and lanthanum.

Since the lower monoalkyl phosphoric acids are not appreciably soluble in benzene or carbon tetrachloride in the presence of water, amyl alcohol was selected as the organic solvent for the extraction reagent. The solvent pair, amyl alcohol and water, was initially considered because the distribution coefficient of the fatty acids in this system was reported to increase uniformly as the size of the carbon chain increased.[7] Subsequently it was found that the distribution of $H_2RPO_4$ in this system followed approximately the same relationship.

The extraction of the metal ions was interpreted in terms of chelate formation.[4] This approach was used in recognition of the functional groups of $H_2RPO_4$. Chelation is believed to take place with the formation of a four-membered ring.

* Present address: Western State College, Gunnison, Colorado, U.S.A.
† Present address: Lawrence Radiation Laboratory, Berkeley, California, U.S.A.
‡ Work performed under contract with the Los Alamos Scientific Laboratory.
§ Symbols used in this paper are defined as follows: R, alkyl; Pr, n-propyl; Bu, n-butyl; Am, n-amyl; Hex, n-hexyl; Oct, n-octyl.

[1] E. M. SCADDEN and N. E. BALLOU, *Analyt. Chem.* **25**, 1602 (1953).
[2] D. F. PEPPARD, G. W. MASON and S. W. MOLINE, *J. Inorg. Nucl. Chem.* **5**, 141 (1957).
[3] D. F. PEPPARD, S. W. MOLINE and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 344 (1957).
[4] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[5] D. A. ELLIS, U.S.A.E.C., DOW-81 (1952).
[6] D. A. ELLIS and R. H. BAILES, U.S.A.E.C., DOW-131 (1955).
[7] R. C. ARCHIBALD, *J. Amer. Chem. Soc.* **54**, 3178 (1932).



Vol.
12
1959/6

## EXPERIMENTAL

*Acid distributions.* Typical liquid–liquid extraction samples were made by adding $HNO_3$, crystalline $H_2RPO_4$, water, and amyl alcohol to a centrifuge tube. The sample was violently shaken for 5 min at 26 ± 2°C and then a portion of each phase taken for analysis. Agitation times from 1 to 10 min made no change upon the distribution of the acids.

The concentrations of both the $HNO_3$ and the $H_2RPO_4$ were obtained experimentally from a pH titration using standardized NaOH solution. In a water solution both the $HNO_3$ and the first acid group of $H_2RPO_4$ were neutralized at approximately pH 4·5, and the second acid group of $H_2RPO_4$ was neutralized at approximately pH 9·5. Amyl alcohol solutions of $H_2RPO_4$ were diluted with a solution of 60 per cent acetone and 40 per cent water to obtain one phase. In this solution the above end-points were slightly displaced. The concentrations of individual acids were obtained by differences in the equivalents of NaOH consumed to these various end-points of the titration curve.

In practice the equilibrated concentration of $HNO_3$ and $H_2RPO_4$ in each phase was calculated from pre-equilibrated concentrations utilizing the distribution coefficients obtained experimentally. For example, the equilibrated concentration of $HNO_3$ in the aqueous phase, $C(1 - \alpha)$, was obtained by the following formulae when equal phase volumes were used.

$$K_d = \frac{[HNO_3]_{(o)}}{[HNO_3]_{(aq)}}; \qquad K_d = \frac{C\alpha}{C(1-\alpha)}; \qquad K_d = \frac{\alpha}{1-\alpha}$$

where $\alpha$ = fraction of $HNO_3$ entering organic phase,
$C$ = pre-equilibrated $HNO_3$ concentration in the water phase.

It was estimated that changes in phase volumes due to the partial transfer of the phases upon equilibration introduced an error of less than 2 per cent. The transfer of water into the organic phase was eliminated by using amyl alcohol which was previously saturated. It was not possible to use water saturated with amyl alcohol because of the possibility of alcoholysis of the pyrophosphate in the hydrolysis step as described in the next paragraph. However, the transfer of amyl alcohol into the aqueous phase was partially compensated by transfer of nitric acid into the organic solvent. The volume of the $H_2RPO_4$ in the organic phase was added to the volume of amyl alcohol used and the concentrations adjusted accordingly. Only 2 ml of each phase was used in each sample, and the analytical determinations of the equilibrated system were restricted to the more concentrated solutions. The difference between the calculated concentrations and the concentrations which were experimentally determinated was less than 2 per cent.

*The distribution coefficients of the metal ions.* A weighed amount of crystalline $H_2RPO_4$ and 1 ml of water were added to a glass-stoppered centrifuge tube. The tube was tightly sealed and heated on a steam bath 12 hr. The change in weight for this process was checked for each sample and was found to be negligible. One millilitre of $HNO_3$, 2 ml of amyl alcohol saturated with water, and 0·005 ml of the radioactive metal ion solution were added. The centrifuge tube was violently shaken for 5 min in a mechanical shaker thermostated at 26 ± 2°C in an air bath. The tube was centrifuged for 2 min, and 1 ml of solution was removed for tracer analysis. Variation of the agitation times from 1 to 10 min made no change in the distribution of the metal. This probably indicated that equilibrium conditions were obtained, and the subject was not investigated further.

The approximate concentrations of the metal ions in the aqueous phase before equilibration were as follows: $Sc^{3+}$ $10^{-3}$ M, $Y^{3+}$ $10^{-6}$ M, and $La^{3+}$ $10^{-6}$ M. However, variation of the concentration of the metal ion over a wide range made no change in the distributions reported. The radioactive Sc and Y were obtained from Oak Ridge National Laboratory in a HCl solution. These were twice fumed to dryness with concentrated $HNO_3$ and then dissolved in 1 M $HNO_3$. Inactive $Y_2O_3$ was added to the carrier free solution of $Y(NO_3)_3$. Lanthanum oxide which was irradiated with slow neutrons by the Los Alamos Scientific Laboratory was dissolved in 1 M $HNO_3$. The radioactive isotopes together with their half-lives are as follows: scandium-46, 85 days; yttrium-91, 59·5 days; and lanthanum-140, 40 hr.

A scintillation counter was used to determine the $\gamma$-activity of the yttrium and lanthanum solutions. A Geiger counter was used to measure the $\beta$-activity of the separated scandium oxalate precipitate. The ratio of radioactivity per unit volume in the organic phase to that in the aqueous phase was taken to be the ratio of the concentrations of the metals and is defined as $K_M$.

*Preparation of the monoalkyl orthophosphoric acids.*[8] The preparation described below was designed to eliminate several classes of impurities in the final product. This was necessary since low concentrations of the metal ions were used to trace the reaction, and correspondingly small amounts of impurities in the reagents could possibly mask the desired reaction.

About 0·55 mole of the monoalkyl dichlorophosphate, $RCl_2PO_2$, was recovered from the reaction of 2 moles of $POCl_3$ and 1 mole of the appropriate alcohol. The excess of $POCl_3$ was used to repress formation of the secondary and tertiary esters. The reaction mixtures were separated into their components by distillation at a pressure less than 0·001 atm and a temperature under 100°C. An unpacked distilling column about 12 in. long was used in the distillation.

Each of the compounds, $RCl_2PO_2$, was hydrolysed with NaOH in the presence of $BaCl_2$ in a large excess of water. The product of the hydrolysis was the sparingly soluble salt, $BaRPO_4$. About 0·55 moles of the dry anhydrous salt was recovered from a corresponding amount of the $RCl_2PO_2$.

The $H_2RPO_4$ was produced by the reaction of $BaRPO_4$ with dilute $H_2SO_4$. The product was separated by repeated extractions of the $H_2RPO_4$ with ether. The ether solution was evaporated at room temperature, and the product was analysed. The $H_2RPO_4$ at this stage was contaminated with 5–10 per cent of the corresponding dialkyl pyrophosphoric acid, $H_2R_2P_2O_7$. This was hydrolysed to the ortho form by treatment with water at 95°C for 12 hr. Dehydration of the $H_2RPO_4$ with silica gel at room temperature over a period of weeks gave a very viscous product. This material was crystallized by using liquid nitrogen as a coolant. The melting points and analyses of the crystalline acids are given in Table 1.

TABLE 1.—MELTING POINTS AND ANALYSES OF THE MONOALKYL ORTHOPHOSPHORIC ACIDS

| Compound | Observed phosphorus content (%) | Calculated phosphorus content (%) | Melting points (°C) |
|---|---|---|---|
| $H_2PrPO_4$ | 22·2 | 22·11 | 35·8–37·3 |
| $H_2BuPO_4$ | 20·0 | 20·11 | 32·0–33·3 |
| $H_2AmPO_4$ | 18·3 | 18·44 | 28·0–29·5 |
| $H_2HexPO_4$ | 16·9 | 17·01 | 7·5– 8·7 |
| $H_2OctPO_4$ | 14·5 | 14·75 | 27·9–29·4 |

The $H_2R_2P_2O_7$ content was determined from pH titrations. Both acid groups of $H_2R_2P_2O_7$ and the first acid group of $H_2RPO_4$ were neutralized at approximately pH 4·5. The second acid group of $H_2RPO_4$ was neutralized at approximately pH 9·5. This, however, did not uniquely identify the $H_2R_2P_2O_7$ since other acids such as $HR_2PO_4$ have titration curves which are similar to the pyro derivative. The $H_2R_2P_2O_7$ was hydrolysed to the corresponding $H_2RPO_4$ by an excess of water at 95°C in 12 hr. It was also possible to regenerate 5–10 per cent $H_2R_2P_2O_7$ by heating the $H_2RPO_4$ in an open vessel for 12 hr.

The reaction between the metal ions; $Sc^{3+}$, $Y^{3+}$ and $La^{3+}$; and a mixture containing $H_2R_2P_2O_7$ and $H_2RPO_4$ was studied by the same procedure used for the purified $H_2RPO_4$. Unreported data indicated that the $H_2R_2P_2O_7$ was a more powerful complexing reagent than the $H_2RPO_4$. It appeared that different reactions were involved in the extraction of $Sc^{3+}$, $Y^{3+}$ and $La^{3+}$ for these two classes of acids.

*Sources of reagents.* In general analytical grade chemicals were used in this work. The reagents used to prepare the $H_2RPO_4$ were Eastman technical-grade butyl alcohol, amyl alcohol, and octyl alcohol; Eastman practical-grade hexyl alcohol; and Baker and Adamson reagent-grade $POCl_3$. Eastman technical-grade amyl alcohol was used as the carrier solvent and was purified by distillation from a solution containing $NaOC_5H_{11}$. Scandium-46 and yttrium-91 were obtained from the Oak Ridge National Laboratory. Spectroscopically pure $La_2O_3$ from Lindsay Light and Chemical Company was irradiated with slow neutrons by the Los Alamos Scientific Laboratory to produce lanthanum-140.

[8] G. M. KOSOLAPOFF, *Organophosphorus Compounds* p. 180. John Wiley, New York (1950).

Vol. 12 1959/6

## RESULTS AND DISCUSSION

A plot of the experimentally determined distribution coefficient, $K_M$, for the metal ions versus the concentration of $H_2RPO_4$ in the amyl alcohol phase is given by Figs. 1–6. The concentration of $HNO_3$ refers to the aqueous phase.

The data were interpreted by the principles outlined by MARTELL and CALVIN.[9] The method depends upon the formation of a neutral non-ionized extractable chelate complex by the metal ion with an acid which is dissolved in the organic phase. The over-all reaction of the extraction is given in equation (1).

$$M^{3+}_{(aq)} + pH_2RPO_{4(o)} = H_{p-3}M(HRPO_4)_{p(o)} + 3H^{+}_{(aq)} \qquad (1)$$

Variation of the activity of any species will shift the activities of the other components according to the equilibrium constant principle. However, activities were not known, so concentrations were used in processing the data. The equations pertinent to this method are given below. Equation (2) defines the stability constants. The coefficient of the hydrogen ion in the over-all reaction must be three in order to obtain a balanced equation; however, $h$ was substituted for this value in the following equations, and the coefficient was determined experimentally.

$$k_M = \frac{[M]_{(o)}}{[M^{3+}]_{(aq)}} \cdot \frac{[H^+]^h_{(aq)}}{[H_2RPO_4]^p_{(o)}} \qquad K_M = K_M \frac{[H^+]^h_{(aq)}}{[H_2RPO_4]^p_{(o)}} \qquad (2)$$

Equation (3) defines the relation of the slope of the appropriate log–log plots in terms of the coefficients of the over-all reaction.

$$p = \frac{\partial \log K_M}{\partial \log [H_2RPO_4]} \quad \text{and} \quad h = \frac{-\partial \log K_M}{\partial \log [H^+]} \qquad (3)$$

where $[H^+]$ is constant — where $[H_2RPO_4]$ is constant

The dependencies of the distribution coefficient indicated by the reported data are given in Table 2.

TABLE 2.—COEFFICIENTS IN THE OVER-ALL REACTION

| Compound | Scandium | | Yttrium | | Lanthanum | |
|---|---|---|---|---|---|---|
| | $p$ | $h$ | $p$ | $h$ | $p$ | $h$ |
| $H_2BuPO_4$ | 2·4 | 2·2 | 3·5 | 1·9 | 3·2 | 1·4 |
| $H_2AmPO_4$ | 2·9 | 2·4 | 3·8 | 2·6 | 4·0 | 2·5 |
| $H_2HexPO_4$ | 3·0 | 2·8 | 4·0 | 2·6 | 3·6 | 2·8 |
| $H_2OctPO_4$ | 2·8 | 3·0 | 4·1 | 3·1 | 4·0 | 2·8 |

The slopes of the lines, $p$, in Figs. 1–6 were determined by the method of least squares using the raw data. The value given in Table 2 is the average of the slopes at the two acid concentrations reported. The hydrogen ion coefficient, $h$, was determined from the data by means of the following variables: the average value of $p$ reported in Table 2, the difference of the intercepts on the log $[H_2RPO_4]$ axis at the two acid concentrations, and the difference in log $[H^+]$.

[9] A. E. MARTELL and M. CALVIN, *Chemistry of the Metal Chelate Compounds* p. 451. Prentice Hall, New York (1952).

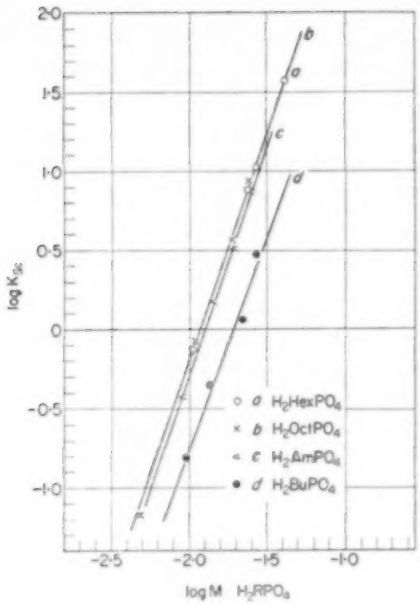



FIG. 1.—Variation of log $K_{Sc}$ with log M $H_2RPO_4$ at 0·274 M $HNO_3$.

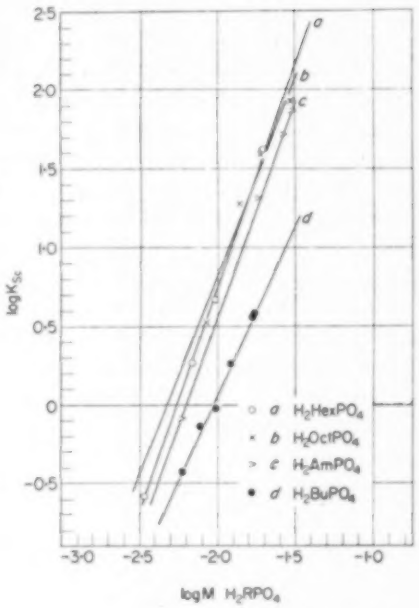



FIG. 2.—Variation of log $K_{Sc}$ with log M $H_2RPO_4$ at 0·115 M $HNO_3$.

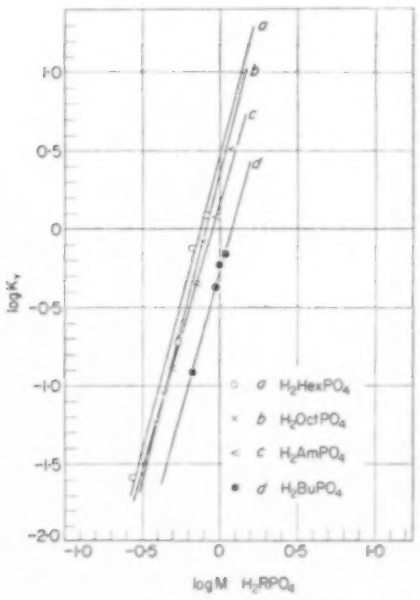



FIG. 3.—Variation of log $K_Y$ with log M $H_2RPO_4$ at 0·274 M $HNO_3$.

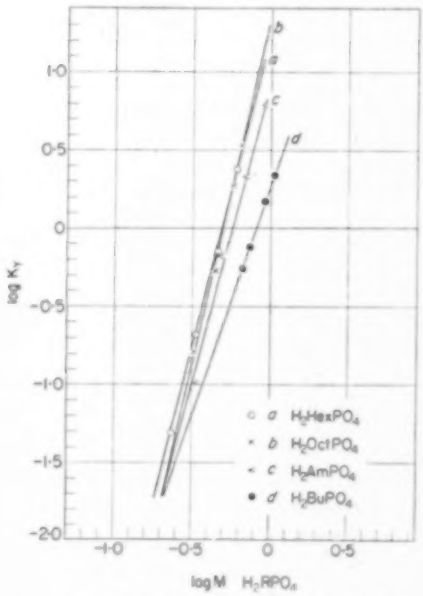



FIG. 4.—Variation of log $K_Y$ with log M $H_2RPO_4$ at 0·143 M $HNO_3$.

Vol. 12 1959/6

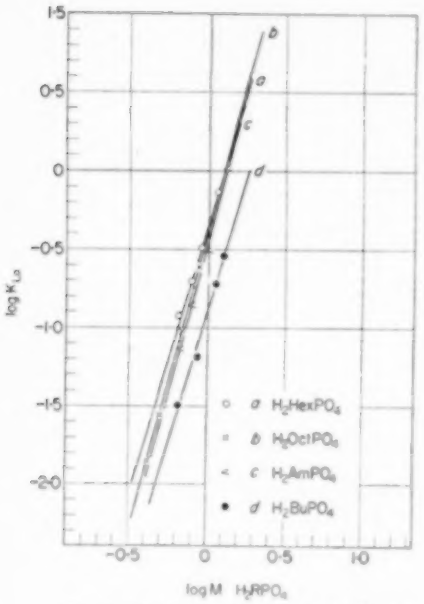



FIG. 5.—Variation of log $K_{La}$ with log M $H_2RPO_4$ at 0·274 M $NHO_3$.

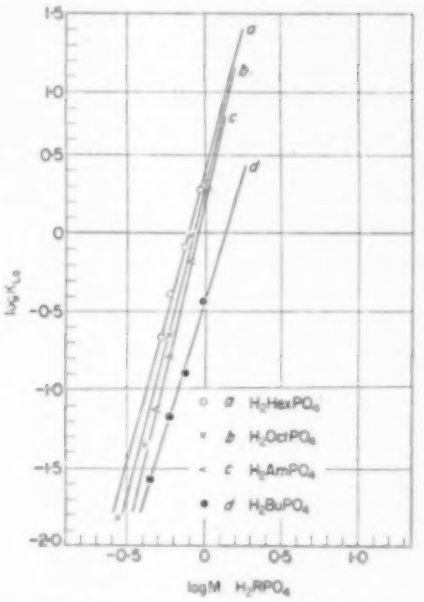



FIG. 6.—Variation of log $K_{La}$ with log M $H_2RPO_4$ at 0·143 M $HNO_3$.

The coefficients of the reaction of the metal ions and $H_2BuPO_4$ do not correspond to any simple mechanism. The assumption that the concentration of the complexed metal ions in water is small compared to the concentration of the non-complexed metal ions in the water probably is not valid, and the simplified treatment implied by the over-all reaction cannot be used for this derivative.

The coefficients obtained for the amyl, hexyl, and octyl phosphoric acids suggest that the following reactions probably occur in the extraction process:

$$Sc^{3+}_{(aq)} + 3H_2RPO_{4_{(o)}} = Sc(HRPO_4)_{3_{(o)}} + 3H^+_{(aq)}$$

$$Y^{3+}_{(aq)} + 4H_2RPO_{4_{(o)}} = HY(HRPO_4)_{4_{(o)}} + 3H^+_{(aq)}$$

$$La^{3+}_{(aq)} + 4H_2RPO_{4_{(o)}} = HLa(HRPO_4)_{4_{(o)}} + 3H^+_{(aq)}$$

The stability constant equations corresponding to the reactions were evaluated for each metal ion using the average coefficients in Table 2 for the amyl, hexyl, and octyl derivatives.

$$k_{Sc} = K_{Sc}\frac{[H^+]^{2\cdot7}}{[H_2RPO_4]^{2\cdot9}} \qquad k_Y = K_Y\frac{[H^+]^{2\cdot8}}{[H_2RPO_4]^{4\cdot0}}$$

$$k_{La} = K_{La}\frac{[H^+]^{2\cdot7}}{[H_2RPO_4]^{3\cdot9}}$$

Each stability constant in Table 3 was obtained from an average of eight independent determinations of log $k_M$. The average deviation of the single determinations from the values of Table 3 was about 0·05.

The concentration of $H_2RPO_4$ required to extract 50 per cent of the metal is a convenient indication of the ability of $H_2RPO_4$ to effect separations.[9] The greater the space between the concentrations the better the separation which may be achieved. A graphical representation of this information is given in Fig. 7.

TABLE 3.—STABILITY CONSTANTS FOR THE EXTRACTION OF THE GROUP IIIA IONS BY $H_2RPO_4$

| Compound | Log $k$ | | |
|---|---|---|---|
| | Scandium | Yttrium | Lanthanum |
| $H_2AmPO_4$ | 3·89 | −1·37 | −2·07 |
| $H_2HexPO_4$ | 4·03 | −1·12 | −1·89 |
| $H_2OctPO_4$ | 4·04 | −1·17 | −1·98 |

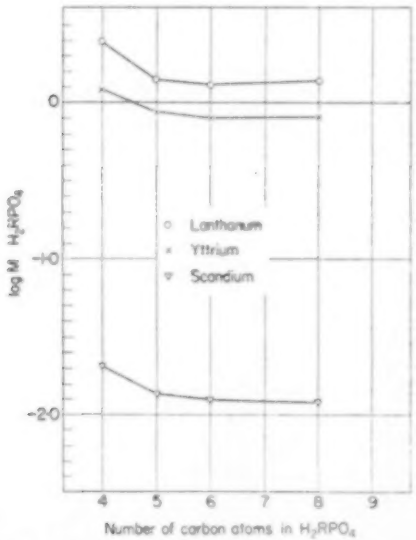



FIG. 7.—Variation of log M $H_2RPO_4$ with the size of the alkyl group at 0·274 M $HNO_3$ and 50 per cent extraction.

## CONCLUSIONS

Limiting values for the stability constant of the extraction reaction between $H_2RPO_4$ and the metal ions are probably reached with the n-amyl derivative. Larger n-alkyl groups apparently have no significant effect on this constant.

The $H_2RPO_4$ could be used to effectively separate scandium and yttrium. However, these compounds do not appear to be applicable to the separation of yttrium and lanthanum. The length of the carbon chain does not appear to affect the ability of the reagents to separate these elements.

Vol. 12 1959/6

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 343 to 381. Pergamon Press Ltd. Printed in Northern Ireland

# NOTES

## The dialysis of polysulphide solutions

(*Received* 20 *March* 1959; *in revised form* 6 *July* 1959)

THE dialysis of polysulphides has been studied only by SPRING and DEMARTEAU,[1] who observed no decomposition during dialysis. From this fact they drew the conclusion that a real chemical bond exists in polysulphides, in place of the labile linkage of colloidal sulphur to sulphide ions as presumed at that time by certain authors.

On the contrary, our first experiments showed that, during dialysis, the polysulphide solutions decomposed and sulphur precipitated. The higher the molecular weight of the original polysulphide solution, the sooner the decomposition took place. It was presumed that changes may occur in the ratio $S_{x-1}/S^{2-}$ during dialysis.

In order to examine this problem, two samples of sodium trisulphide solutions ($Na_2S + 2S$) were prepared and the ratio $S_{x-1}/S^{2-}$ was determined in the solutions.* Subsequently, one of the solutions was subjected to dialysis. During dialysis, samples were withdrawn at short intervals and the ratio $S_{x-1}/S^{2-}$ established. With the other solution, the duration of dialysis was appreciably longer. The results are summarized in Table 1.

TABLE 1

| Duration of dialysis (hr) | Ratio $S_{x-1}$-sulphur/$S^{2-}$-sulphur | |
|---|---|---|
| | Solution I | Solution II |
| 0 | 1·93 | 2·09 |
| 1 | 2·18 | — |
| 1·5 | 2·55 | — |
| 2 | 2·76 | — |
| 5·5 | — | 3·71 |
| 6·5 | — | 3·92 |
| 7 | — | decomposed |

$\underbrace{S_x, S^{2-}, (S_2O_3^{2-})}$

$+ H_3BO_3 + KCN$ boiling

$H_2S$, (HCN) oxidized to sulphuric acid and titrated with sodium hydroxide

$SCN^-$, $(S_2O_3^{2-})$ the thiocyanate is titrated iodometrically.[3]

* The analyses were carried out as described earlier.[2] The method is shown by the scheme:

[1] W. SPRING and J. DEMARTEAU, *Bull. Soc. Chim. Fr.* **1**, 314 (1889).
[3] E. SCHULEK and E. KÖRÖS, *Acta Chim. Hung.* **3**, 111 (1953).
[5] E. SCHULEK, *Z. Anal. Chem.* **62**, 337 (1923).

The data of Table 1 show that with the progress of dialysis the ratio $S_{x-1}/S^{2-}$ continually rises until pentasulphide is formed in the solution ($S_{x-1}/S^{2-} = 4$), when the solution decomposes with precipitation of sulphur.

A solution approximately corresponding to trisulphide was also prepared from sodium hydroxide and sulphur (sodium hydroxide was in excess), in order to examine whether the ratio $S_{x-1}/S^{2-}$ does not rise above 4 when dialysis is carried out in an alkaline solution. The results obtained are presented in Table 2.

TABLE 2

| Duration of dialysis (hr) | Ratio of $S_{x-1}$–sulphur/$S^{2-}$–sulphur |
|---|---|
| 0 | 2·2 |
| 5·5 | 5·4 |
| 7·0 | 5·7 |

It can be seen that after 7 hr of dialysis the ratio $S_{x-1}/S^{2-}$ attained the value of about 5·7. However, on allowing the solution to stand for several hours under pentane, the solution decomposed with precipitation of sulphur.

In our dialysis measurements, we made use of the closed dialysis apparatus shown in Fig. 1. By this technique, it was possible to protect the solutions from air. Throughout the experiments, 50 ml

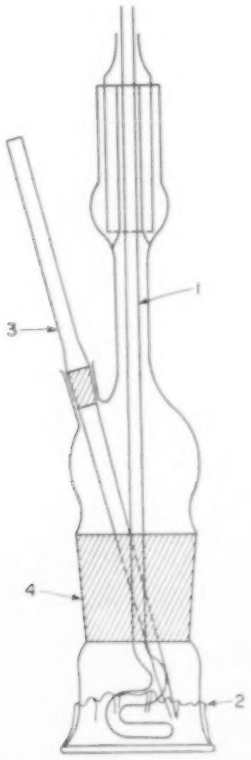



FIG. 1.—Glass dialysis apparatus.
1—stirrer; 2—cellophane membrane; 3—pipette with ground joint, for taking out samples, 4—ground joint.

Vol. 12 1959/6

portions of solution were transferred into the dialysis flask and pentane poured on the surface of the liquid in a 1–2 cm thick layer. The external vessel contained 12 l. of distilled water which was changed each 30 min.

*Discussion of Results*

The dialysis experiments too indicate that in an aqueous solution sulphide ions are capable of binding only four sulphur atoms. Under such conditions, the maximum to be expected is the formation of pentasulphide.

The regular rise of the ratio $S_{x-1}/S^{2-}$ during dialysis can be interpreted as follows. In the reaction sulphur-sulphide, as a first step, the sulphur ring or sulphur chain is split by sulphide ions. Subsequently, sulphide ions form pentasulphide with four sulphur atoms.* Consequently, when a quantity of sulphur sufficient only for the formation of trisulphide is added to sulphide, unreacted sulphide will remain in the solution, although the mean value of the ratio $S_{x-1}/S^{2-}$ will be equal to 2; it is impossible to make any distinction between "two types" of sulphide.

In the course of dialysis, $S^{2-}$ of smaller ionic weight will diffuse more quickly. Thus, the content of $S_x^{2-}$ of the solution in the dialysis vessel will rise until units of $S_5^{2-}$ will remain almost exclusively. The decomposition of $S_5^{2-}$ is due to the decrease of pH caused by the diminished concentration of sulphide ion. This appears probable also in the case of trisulphide solutions prepared with excess alkali, although polysulphides apparently higher than $S_5^{2-}$ form as intermediates. It appears most probable that these solutions of polysulphide had already decomposed and the colloidal sulphur, as decomposition product, was measured by us together with intact polysulphide, since the method of SCHULEK measures all sulphur of zero oxidation number.[4]

It can also be presumed, however, that actually $S_5^{2-}$ ions exist in the trisulphide solution and these hydrolyse according to the equation

$$2S_5^{2-} + H_2O \leftrightharpoons S_5^{2-} + HS^- + OH^- \qquad (1)$$

or, in general:

$$2S_x^{2-} + H_2O \leftrightharpoons HS^- + OH^- + S_{2x-1}^{2-} \qquad (2)\dagger$$

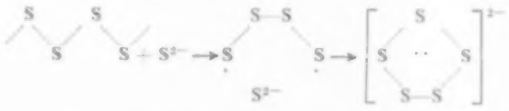
This hydrolysis is promoted by the higher diffusion rate of $HS^-$ and $OH^-$ ions. Consequently, the solution undergoing dialysis is enriched in $S_5^{2-}$ ions until these latter decompose, due to the decreasing pH.

The results obtained point out that the existence of a constant dynamical equilibrium could be considered in polysulphide solutions and it must be presumed that polysulphides of various $x$-values may convert into each other, owing to hydrolysis.

E. SCHULEK
E. KÖRÖS
L. MAROS

*Institute of Inorganic and Analytical Chemistry*
*L. Eötvös University*
*Budapest*

* In our opinion the pentasulphide formed has a ring structure of extreme lability



This assumption however must be supported by further investigations.

† In our opinion, the reaction described by equation (2) can be considered as the first step of the process

$$S_x^{2-} + H_2O \rightarrow S_2O_3^{2-} + H_2S \qquad (4)$$

suggested earlier for the hydrolysis of polysulphides.[5] The further hydrolysis of the formed higher polysulphides takes place to an appreciable extent only at higher temperature.

[4] E. SCHULEK, *Z. Anal. Chem.* **65**, 352 (1924/25).
[5] E. SCHULEK, E. KÖRÖS and L. MAROS, *Acta Chim. Hung.* **10**, 291 (1956).

## The separation and estimation of nitro and non-nitro (nitrato) complexes of nitrosylruthenium in nitric acid solution by paper chromatography

(*Received* 31 *July* 1959)

In the study of the nitrato complexes of nitrosylruthenium,[1] it was found that paper chromatography, employing a relatively fast-moving eluting solvent, could be used to give approximate estimates of the compositions of solutions of these complexes in nitric acid. Methyl isopropyl ketone was found to be a suitable eluting solvent.[2] In subsequent work, the results of which have been reported,[3] refinement of the experimental technique has improved both the resolution and the reproducibility of the chromatograms.

The study of nitrosylruthenium nitrato complexes in nitric acid solution is important because they occur in process solutions which arise from the dissolution of irradiated uranium in nitric acid. Such solutions[4] also contain nitro complexes of nitrosylruthenium.[5,6]

The isolation and study of these two classes of nitrosylruthenium complexes, viz. those with nitro groups and those without nitro groups, has shown that they possess widely differing properties in processes such as solvent extraction, oxidation and precipitation.[7] A method that would permit their separate estimation in solutions of irradiated material (i.e. in the presence of other fission products) is desirable. This has been achieved by employing eluting solvents towards which the two classes of complexes behave in a substantially different manner. Separate aliquots of the solution under test are examined by paper chromatography in which methyl isopropyl ketone (MIPK) and dibutyl cellosolve (DBC) are the eluting solvents. Brief reference was made to this method in a paper[7] to the Geneva Conference of 1958.

While MIPK has been successfully used to resolve the (RuNO) nitrato (non-nitro) complexes present in certain solvent solutions,[1] differences in behaviour between these and the (RuNO) nitro complexes, both in MIPK and in DBC elution, are less pronounced when they are present in a TBP phase and the method described has not yet been suitably modified to apply to organic phases.

### *Choice of Eluting Solvent*

It has been known for some time that the triple-ether, dibutyl carbitol (butex), will extract (RuNO) complexes, but, with this solvent, selectivity is poor[8] and there is only partial separation of the two classes of complexes; also, because of the viscosity of this solvent, the time of elution is long. On the other hand, with the mono-ether, dibutyl ether, extraction of both classes of complexes is low, and there is little movement of ruthenium beyond the applied spot. The di-ether, dibutyl cellosolve, was therefore tested and found to be satisfactory in that while the (RuNO) nitro complexes remained on the applied spot, the higher nitrato complexes (with $NO_3 : Ru > 3 : 1$) were selectively eluted with $R_F$ values between 0·2 and 0·6.

Methyl isopropyl ketone was known, from previous work,[2] to be suitable for the resolution of the individual (RuNO) nitrato (non-nitro) complexes. Other solvents that were tried and rejected on the grounds of either poor resolution or non-selectivity between the nitro and non-nitro complexes, were methyl ethyl ketone, methyl isobutyl ketone (hexone), cyclohexanone, diethyl carbitol, diethyl cellosolve, 20 per cent butex in dibutyl cellosolve, and tributyl phosphate (TBP) diluted with odourless kerosene, carbon tetrachloride or xylene.

[1] P. G. M. Brown, J. M. Fletcher and A. G. Wain, U.K.A.EA. Document, A.E.R.E. C/R 2260 (1957).
[2] A. G. Wain, P. G. M. Brown and J. M. Fletcher, *Chem. & Ind.* 18 (1957).
[3] J. M. Fletcher, P. G. M. Brown, E. R. Gardner, C. J. Hardy, A. G. Wain and J. L. Woodhead, *J. Inorg. Nucl. Chem.* **12**, 154 (1959).
[4] A. Naylor. U.K.A.E.A. Document, IGR-TN/W-1042 (1959).
[5] J. M. Fletcher, I. L. Jenkins, F. M. Lever, F. S. Martin, A. R. Powell and R. Todd. *J. Inorg. Nucl. Chem.* **1**, 378 (1955).
[6] P. G. M. Brown, Nitro complexes of nitrosylruthenium. *J. Inorg. Nucl. Chem.* In press (1960).
[7] P. G. M. Brown, J. M. Fletcher, C. J. Hardy, J. Kennedy, D. Scargill, A. G. Wain and J. L. Woodhead, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, Vol. 17, p. 118. United Nations, New York (1959).
[8] G. W. C. Milner and L. Salmon, U.K.A.E.A. Document, A.E.R.E. C/M 119 (1951).

Vol. 12 1959/6

*Experimental*

The recommended experimental method, which is described in detail in earlier papers,[2,3] is summarized here. Of the solution under test, which should be aged at least 2 hr, 0·001 ml is applied to the bottom section (section 1) of a previously dried Whatman No. 41 (type CRL/1) paper strip that has been marked in 17 × ½ cm sections. The whole is immediately placed in a closed 600 ml beaker containing 1 cm depth of the solvent, and the chromatogram is formed by upward elution in an atmosphere of the solvent. The times of elution to the top of the strip at room temperature are about 13 and 27 min respectively for MIPK and DBC. After drying, the paper strip is cut into the 17 sections and each one is $\beta$ or $\gamma$ counted for $^{106}$Ru: a histogram representing the distribution of ruthenium along the paper strip is constructed from these results.

Small points of technique that affect the resolution of the individual complexes on the chromatogram are summarized below. For the best results: (a) the volume of liquid applied to the paper should not exceed 0·005 ml (see Fig. 1 and Ref. 1, Fig. 1), and this should be applied in the form of

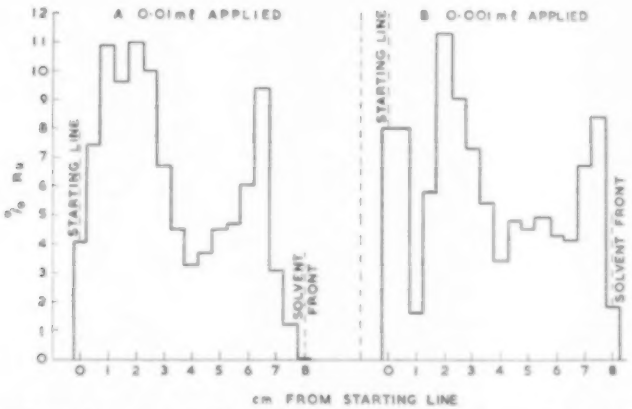



FIG. 1.—Paper chromatograms for (RuNO) nitrato (non-nitrato) complexes at equilibrium in 3 M $HNO_3$ containing 1·25 M $UO_2(NO_3)_2$.

a band rather than a spot; (b) the applied liquid should not be allowed to dry before running the chromatogram; (c) liquids of high nitric acid concentration should be diluted to 3 M $HNO_3$ immediately before application to the paper, to prevent attack on the solvent or the paper by nitric acid; (d) the paper should be dried before use; (e) the solvent should be pre-equilibrated with 3 M $HNO_3$ free from dissolved oxides of nitrogen, and should not be allowed to stand more than 30 min before running the chromatogram; (f) DBC should be centrifuged after equilibration with 3 M $HNO_3$, but this is not so important with MIPK; (g) before inserting the paper strip, the solvent should be left for at least 15 min in the closed beaker to allow the solvent to saturate the atmosphere above its surface; (h) the time of elution should be short, hence the use of Whatman No. 41 paper; (i) the chromatogram should be dried immediately after elution has finished.

*Results*

The characteristic chromatograms given by the two classes of (RuNO) complex have been given in earlier papers.[5,6] Table 1 gives $R_F$ values for individual complexes with MIPK and DBC elution. Figs. 2, 3 and 4 of Ref. 3 illustrate respectively typical chromatograms obtained with solutions of the nitrato (non-nitro) complexes in 3 M, 7·8 M and 14·5 M $HNO_3$ both with MIPK and DBC elution. Figs. 5 and 6 of Ref. 6 illustrate MIPK elution of typical solutions of (RuNO) nitro complexes in 3 M $HNO_3$: in DBC elution the nitro complexes do not move beyond section 2 of the chromatogram.

These characteristic chromatograms are affected slightly by the presence of uranium in the solution; with MIPK elution, the presence of U at the solvent front causes the $R_F$ values for the higher nitrato (Fig. 1 and Ref. 1, Fig. 7) and dinitro complexes to drop by about 10 per cent; with DBC elution the effect is negligible.

TABLE 1.—THE BEHAVIOUR OF (RuNO) COMPLEXES IN PAPER CHROMATOGRAPHY

| (RuNO) Complex | $R_F$ value with MIPK elution | | $R_F$ value with DBC elution |
|---|---|---|---|
| | $HNO_3$ | $HNO_3$ + 300 g/l U | |
| Tetra- and penta-nitrato | 0·9–1·0 | 0·85–0·9 | 0·2–0·7 |
| Trinitrato | 0·4–0·9 | 0·4–0·85 | <0·15 |
| Dinitrato | ~0·25 | ~0·25 | |
| Mononitrato | <0·1 | <0·1 | |
| Dinitro | 1·0 | ~0·9 | |
| $NO_2$ : Ru = 3 : 1 | ~0·5 | ~0·45 | |
| $NO_2$ : Ru > 3 : 1 | 0·2 | 0·2 | |

TABLE 2.—THE PERCENTAGE OF RUTHENIUM PRESENT AS HIGHER NITRATO COMPLEXES OF NITROSYL-RUTHENIUM AT EQUILIBRIUM IN NITRIC ACID–NITRATE SYSTEMS

| Total nitrate concentration (M) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| % Ru as tetra- and penta-nitrato complexes ($z$) | 2 | 4 | 8 | 15 | 23 | 33 | 42 | 51 | 57 | 62 |

Vol. 12 1959/6

TABLE 3.—THE USE OF PAPER CHROMATOGRAPHY TO DETERMINE THE COMPOSITIONS OF CERTAIN SYNTHETIC SOLUTIONS CONTAINING (RuNO) NITRATO AND NITRO COMPLEXES IN NITRIC ACID

| Synthetic solution | % Ruthenium as | | | | $x - y + \frac{100}{z}y$ |
|---|---|---|---|---|---|
| | (RuNO) higher nitrato + dinitro ($x$) | (RuNO) higher nitrato ($y$) | (RuNO) dinitro ($x - y$) | Higher nitrato in non-nitro system ($z$)* | |
| *Separate species* | | | | | |
| 3 M $HNO_3$ + nitrato | 7·7 | 7·5 | | 8 | 94 |
| 3 M $HNO_3$ + nitro | 43·7 | 0 | 43·7 | | 43·7† |
| 3 M $HNO_3$ + 1·25 M $UO_2(NO_3)_2$ + nitrato | 27·0 | 24·1 | | 25 | 97 |
| *Mixed species* | | | | | |
| 2 M $HNO_3$ | 15·0 | 3·5 | 11·5 | 4 | 99 |
| 3 M $HNO_3$ | 19·0 | 7·3 | 11·7 | 8 | 103 |
| 3 M $HNO_3$ + 1·25 M $UO_2(NO_3)_2$ | 42·3 | 16·2 | 26·1 | 25 | 91 |

* Interpolated from values in Table 2.

† Solutions containing only nitro complexes do not contain 100 per cent as the dinitro complex (usually ~50 per cent).

In solutions ~3 M in $HNO_3$, most of the fission products other than ruthenium remain on section 1 of the chromatogram. Zr and Nb, being both solvent-extractable and $\gamma$ emitters, might be expected to interfere with these determinations, but do not move beyond section 2 with DBC elution: with MIPK they can appear with $R_F$ values as great as 0·6, but they do not contaminate the ruthenium on the solvent front.

Ruthenium present in valency states other than (RuNO) III, e.g. Ru III and Ru IV, does not move beyond section 2 with either MIPK or DBC elution.

*Method*

A combination of MIPK and DBC elution makes possible the following method for the separate estimation of the (RuNO) nitro and nitrato (non-nitro) complexes in mixtures of the two classes of complexes in nitric acid solution.

Let $x$ = per cent Ru in MIPK elution with $R_F > 0{\cdot}9$.

Let $y$ = per cent Ru in DBC elution with $R_F > 0{\cdot}15$.

Then $x - y$ = per cent Ru present as the (RuNO) dinitro complex.

Let $z$ = per cent Ru present as higher nitrato complexes ($NO_3$ : Ru > 3 : 1) for a non-nitro system in the aqueous conditions that apply (see Table 2).

On the assumption that the (RuNO) dinitro complex is the only species not in equilibrium with the nitrato complexes,

100 $y/z$ = per cent Ru present as (RuNO) nitrato (non-nitro) complexes, and $x - y + 100\ y/z$ should equal 100. Table 3 gives results for separate and mixed classes of complexes.

This method is applicable to the analysis of aqueous process solutions from chemical separation plants, designed to separate plutonium and fission products from irradiated uranium by solvent extraction in nitric acid systems, and has been successfully used by NAYLOR[4] at Windscale.

*Atomic Energy Research Establishment*
*Harwell, Didcot, Berks*

A. G. WAIN
P. G. M. BROWN
J. M. FLETCHER

ol.
12
9/60

## Molybdic acid and its organic complexes—III

## Some studies on the acid nature molybdic oxide and its solubility in polyhydroxy alcohols

(*Received* 12 *August* 1959)

THE solubility of molybdic oxide $MoO_3$ in alkali and mineral acids has been studied by many workers.[1] It is generally agreed that dissolution of a stoicheiometric excess of molybdic oxide in alkalis (or normal molybdates) produces polymolybdates[1,2] which may be crystallized from solution. Solution in mineral acids, according to many authors, produces molybdenyl compounds of the type $MoO_2SO_4$, $MoO(SO_4)_2$. JONES,[3] however, in more recent work suggests that equilibrium in solution is more complex and is of the form

$$xMoO_3 + 2H^+ \rightleftarrows [(MoO_2)(MoO_3)_{x-1}]^{2+} + H_2O$$

Much needless confusion exists in the literature concerning the solubility of molybdic oxide in pure water. Preliminary work in this College in connexion with another project indicated that a reasonably strong acid of pH 2–3 was produced readily by shaking pure crystalline anhydrous $MoO_3$ in water. KILLEFFER and LINZ,[1] however, state that $MoO_3$ dissolves only very slowly to produce a solution of pH 4·0–4·5.

[1] D. H. KILLEFFER and A. LINZ, *Molybdenum Compounds—Their Chemistry and Technology*. Interscience, New York (1952).
[2] J. BYE, Thesis, Paris (1945).
[3] M. M. JONES, *J. Amer. Chem. Soc.* **76**, 4233 (1954).

*Experimental*

AnalaR crystalline $MoO_3$ was purified by sublimation. This material contains no ammonia. Most solubility experiments were performed at 19°C.

Since the time of contact extended over two weeks "Lusteroid" plastic test tubes of capacity 50 ml were used. Tubes containing 250 mg $MoO_3$ and 40 ml of fresh distilled water (or solution) were agitated continuously on a mechanical shaker. For experiments at higher temperatures, where the period of contact was much shorter, hard glass conical flasks were used.

All conductivity measurements were made using a Mullard Conductivity Bridge operating in the most sensitive range with a cell of constant 1·54. Measurements of pH were made on a Cambridge pH meter using a glass–calomel electrode system calibrated by buffers complying with modern standards. Absorption measurements were made on a Hilger Uvispek Absorptiometer using 0·5 cm quartz cells.

The molybdenum concentrations were determined colorimetrically using gallic acid, buffered with sodium acetate. Gallic acid forms a stable yellow-brown complex with molybdate.[4] Full details of this method by BUCHWALD and RICHARDSON[4] will be published elsewhere. By using 2 ml samples of solution for the molybdate determination the concentration of polyhydroxy alcohol in the analytical mixture was reduced to well below the limit of interference. Checks were made periodically where the molybdate concentration was determined either gravimetrically, or conductometrically against standard NaOH; the results were in agreement within experimental error.

*Results and Discussion*

(a) *The acidic nature of aqueous solutions of molybdic oxide*

A solution of molybdic oxide in water was prepared by boiling 1 g of $MoO_3$ in 200 ml of water for 3 hr. Aliquots of the cooled solution, clear to the naked eye, were then titrated either conductometrically or potentiometrically with 0·1 N NaOH. The results of these experiments are shown in Fig. 1. Curves of similar shape were obtained on titration of a similar quantity of molybdic oxide

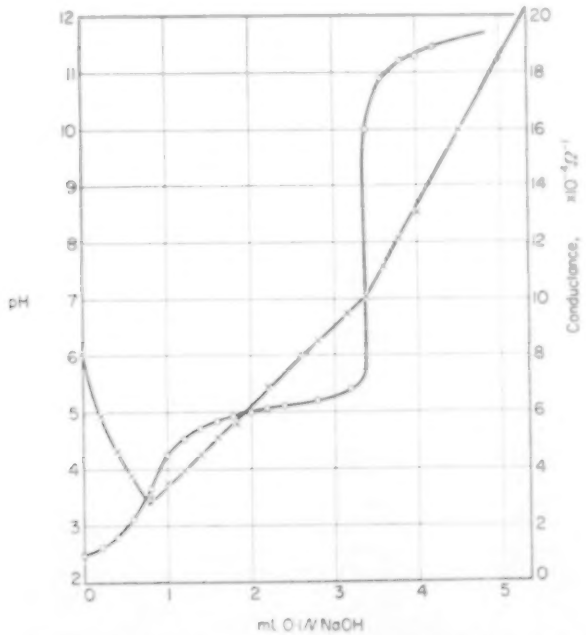



FIG. 1.—Potentiometric (●) and conductometric (×) titration of 20 ml boiled $MoO_3$ solution with sodium hydroxide.

[4] H. BUCHWALD and E. RICHARDSON, *Chem. & Ind.* 753 (1959).

Vol. 12 1959/6

solution (of an almost identical molybdate concentration) prepared by agitating 0·25 g of molybdic oxide with 40 ml of distilled water for two weeks at room temperature. The pH of the molybdic oxide solutions prepared by boiling and by agitating at room temperature were 2·48 and 2·54 respectively. Presumably, therefore, values of 4·5 quoted in the literature[1] were obtained by dissolution of impure

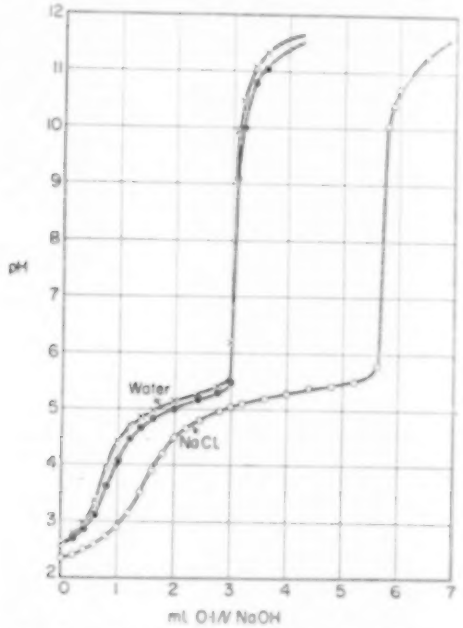



FIG. 2.—Effect of sodium chloride on the solubility of $MoO_3$. Potentiometric titration of 20 ml $MoO_3$ solution prepared by boiling with 0·1 M NaCl (○); with water (×) and with water then made 0·1 M w.r.t. NaCl by addition of solid (●). All 20 ml aliquots.

$MoO_3$ containing ammonia or other alkali which produced a buffering effect. From these results it can clearly be seen that molybdic oxide in dilute solution behaves as a fairly strong acid. For comparison 1 g of molybdic oxide was boiled for 1 hr with (a) distilled water (b) 0·1 M sodium chloride. The results obtained on potentiometric titration with 0·1 N NaOH of 20 ml samples of these centrifuged solutions are shown in Fig. 2. Addition of sodium chloride increases the solubility of the molybdic oxide but the general shape of the titration curve is unaltered and although the pH of the solution is low the sodium chloride does not induce the formation of molybdenyl compounds. This is confirmed by studies of the U.V. absorption spectra (Fig. 3). The spectrum of the saline solution is essentially similar to that of the aqueous solution.

Molybdic oxide solution prepared either by boiling or in the cold produced a glass exhibiting conchoidal fracture on evaporation at room temperature.

KILLEFFER and LINZ[1] state that molybdic oxide dissolves to a slight extent on long standing in water. Preliminary work, however, showed that an acid solution was obtained immediately on shaking $MoO_3$ with water. Since the solution produced is a fairly strong acid and is reasonably dilute, the rate of dissolution may easily be followed by noting the variation of conductance with time of a continuously agitated suspension of $MoO_3$ in water. The conductance of this suspension was found to vary almost linearly with time during the initial dissolution period and after 140 min the conductance was $2·7 \times 10^{3}$, in comparison with $8·25 \times 10^{3}$ for a fully saturated solution under the same conditions. Samples from this solution titrated conductometrically or potentiometrically with NaOH gave breaks at the same Na : Mo ratios as in Fig. 1. Thus it is evident that when $MoO_3$ dissolves in water interaction with the solvent occurs either directly or within a short period. Moreover, when a clear saturated solution of $MoO_3$ is prepared by boiling, no precipitation of solid or even turbidity occurs on cooling.

It seems reasonable to suppose that molybdic oxide is in fact an anhydride of some molybdic acid but that this is not the monohydrate or dihydrate discussed in the literature. The general shape of the conductivity and pH curves and the particular value of these quantities at a given concentration,

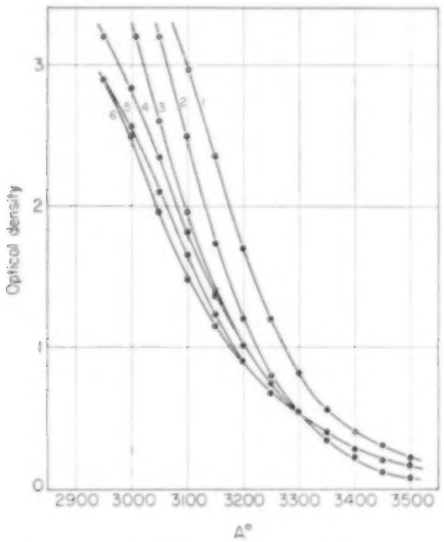



FIG. 3.—Absorption spectra of $MoO_3$ solution containing various compounds. 1—NaCl (as Fig. 2); 2—mannitol (as Fig. 4); 3—erythritol (as Fig. 4); 4—aqueous and glycerol solution (as Fig. 4); 5—boiled $MoO_3$ solution (as Fig. 1); and 6—glucose (as Fig. 4).

Vol. 12 1959/6

together with the fact that both materials yield the same product on evaporation at room temperature, suggest that molybdic oxide solution is similar in most characteristics to molybdic acid prepared by ion exchange and described in a previous paper in this series.[5]

(b) *The effect of polyhydroxy compounds on the solubility of* $MoO_3$

It is generally agreed that polyhydroxy compounds increase the solubility of molybdic oxide, but much of the information presented in the literature was obtained by gravimetric studies on $MoO_3$ often of doubtful purity.[1] The development of colorimetric methods for the determination of molybdenum in solution has considerably facilitated solubility studies.

The effect of several polyhydroxy alcohols on the solubility of $MoO_3$ is shown in Fig. 4. Similar curves were obtained on plotting either pH or conductance against time. Mannitol, which is known to form a $2MoO_3{:}C_6H_{14}O_6$ complex with molybdic acid, has the greatest effect on both the rate of solution of $MoO_3$ and the equilibrium concentration of molybdic acid formed. Glycerol, which does not complex with molybdic acid,[7] affects neither the rate of solution nor the equilibrium solubility. The enhanced solubility is presumably due to complex formation rather than to any general effect caused by the presence of hydroxyl groups.

Complex formation between tungstic acid and α hydroxy acids involves a degradation of the polytungstic acid.[8] This process may be followed by studying the shift in the characteristic absorption edge of the tungstate from 3600 to 2700 Å after addition of the organic acid. Spectra were taken therefore of clear aliquots from the tubes shaken for 16 days, to investigate if a similar breakdown in the molybdic acid had occurred on complex formation with the polyhydroxy compounds (Fig. 3). No appreciable shift in the characteristic absorption edge was found and the slight shift observed with

[5] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **9**, 267 (1959).
[6] H. FREY, *Ann. Chim.* **18**, 1 (1943).
[7] E. RICHARDSON, *J. Inorg. Nucl. Chem.* **9**, 273 (1959).
[8] E. RICHARDSON, In press.

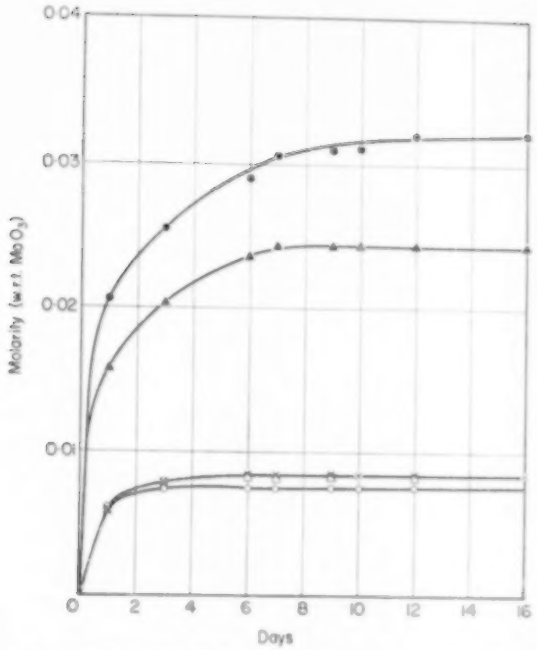



FIG. 4.—Effect of polyhydroxy compounds on the solubility of $MoO_3$.
○ glucose; × water; □ glycerol; ▲ erythritol; ● mannitol.

mannitol and erythritol was towards the visible. A shift in this direction is normally due to aggregation. Degradation of the molybdic acid does not occur, therefore, on complexing with mannitol or erythritol.

The mannitol and erythritol complexes produced in the solubility studies were similar in properties to those obtained from molybdic acid prepared by ion exchange.[7] Both are strong acids, the limiting pH of the solutions produced by dissolution being 1·75 and 1·94 respectively in comparison with 2·54 for that of the aqueous solution.

E. RICHARDSON

*College of Further Education*
*Whitehaven, Cumberland*

---

## On the protonation of complexes

(*Received* 12 *August* 1959)

THE complex forming agents, both anions and dipolar molecules, can combine with hydrogen ions, i.e. both types of ligands can be regarded as Lewis bases. Consequently a competition must arise between the central metal ion and the protons. Thus, on acidifying the solution of a complex ion or molecule the complex decomposes at an acidity determined by its stability constant and by the value of the acidic dissociation constant of the ligand. The study of the effect of acids on the decomposition of the complexes supplies information about the stability constants of the complexes, especially of the protonated complexes.

In the following, we deal with the chelates in which the ratio of ligand to metal ion is 1 : 1. The decomposition of these chelates can be expressed by the following function

$$K(H^+) = \frac{\sum_{0}^{z-1} [MH_n Y^{n+m-y}]}{[M^{m+}][Y^{z-}]} = \frac{[MY^{m-y}]}{[M^{m+}][Y^{y-}]} + \frac{[MHY^{m+1-y}]}{[M^{m+}][Y^{y-}]} + \ldots + \frac{[MH_{z-1}Y^{m+z-1-y}]}{[M^{m+}][Y^{y-}]} \quad (1)$$

In the above expression $m$ denotes the valence of the central ion $M$ of co-ordination number $N$, $n$ is the number of protons taken up by the chelate, $y$ the number of acidic character groups while $z$ is the number of function groups of the polydentate ligand $Y$.

As can be seen the first member of the above expression is equal to the stability constant of the

TABLE 1.—$t = 20°C$; $I = 1$

| | Fe(III)EDTA | Fe(III)DCYTA |
|---|---|---|
| $K_{H,0}$ | $1{\cdot}68 \cdot 10^{24}$ | $3{\cdot}0 \cdot 10^{27}$ |
| $K_{H,1}$ | $1{\cdot}80 \cdot 10^{13}$ | $1{\cdot}0 \cdot 10^{17}$ |
| $K_{H,2}$ | $5{\cdot}26 \cdot 10^{3}$ | $9{\cdot}0 \cdot 10^{10}$ |
| $K_{H,3}$ | — | $8{\cdot}7 \cdot 10^{7}$ |

normal (*non-protonated*) complex ($K_{H,0}$), the further members only differ from the constants of protonated complexes

$$K_{H,n} = \frac{[MH_n Y^{n+m-y}]}{[M^{m+}][H_n Y^{n-y}]} \quad (2)$$

in that the nominator $[Y^{y-}]$ is written instead of $[H_n Y^{n-y}]$. Expressing the concentration of $MH_n Y^{n+m-y}$ from equation (2) and substituting into equation (1) we get

$$K(H^+) = \sum_{0}^{z-1} K_{H,n} \frac{[H_n Y^{n-y}]}{[Y^{y-}]} = K_{H,0} + K_{H,1} \frac{[HY^{1-y}]}{[Y^{y-}]} + \ldots + K_{H,z-1} \frac{[H_{z-1}Y^{z-1-y}]}{[Y^{y-}]} \quad (3)$$

Considering that

$$\frac{[H_n Y^{n-y}]}{[Y^{y-}]} = \frac{[H^+]^n}{K_{z-1}K_{z-1}\cdots K_{z-n+1}}$$

where K is the acidic dissociation constant ($K_{z-1} = 1$) — $K(H^+)$ can be written as follows:

$$K(H^+) = \sum_{0}^{z-1} K_{H,n} \frac{[H^+]^n}{K_z K_{z-1}\cdots K_{z-n+1}} = K_{H,0} + K_{H,1} \frac{[H^+]}{K_z} + \ldots + K_{H,z-1} \frac{[H^+]^{z-1}}{K_z K_{z-1}\cdots K_2} \quad (4)$$

Three kinds of behaviour can be distinguished:

The first case ($n = 0$) means that the uptake of one proton results in splitting off the ligand, therefore the formation of a protonated complex in detectable amount is excluded. Plotting $K(H^+)$ as a function of hydrogen ion concentration one obtains a straight line parallel to the abscissa. $K(H^+) = K_{H,0}$.

If $n = 1$, besides the existence of the normal complex the existence of one protonated complex must be taken into account. However, the uptake of the second proton results in the total decomposition of the chelate, i.e. the concentration of the other protonated complexes is negligible. Plotting $K(H^+)$ as a function of the concentration of the hydrogen ions we get a straight line the axial intercept of which is equal to $K_{H,0}$ while $K_{H,1}$ can be calculated from the slope of the line.

If $n > 1$ the existence of more protonated complexes must be considered. In this case the change of $K(H^+)$ as a function of the hydrogen ion concentration is expressed by a curve of higher order. The stability constants of different complexes can be obtained by a simple mathematical analysis of $K(H^+)$.

Vol. 12 1959/60

Thus any method (spectrophotometry, polarography etc.) of determination of the ratio of the sum of the concentration of complexes to the concentration of free central ions is suitable for evaluation of the stability constants of the normal and protonated metal chelates.

This method is simpler and applicable at higher acidity than earlier methods.[1,2]

Table 1 contains data for Fe(III)-ethylenediaminetetraacetic acid and Fe(III)-1,2-diamino cyclohexanetetraacetic acid systems, obtained by spectrophotometric measurements.

In the calculations the basic property of the tertiary nitrogens of the complex forms[3] was taken into account.

Details will be published in *Acta Chim. Hung.*

*Institute for Inorganic and Analytical Chemistry*
*University of Szeged*

M. T. Beck
S. Görög

[1] R. K. Cannan and A. Kibrick, *J. Amer. Chem. Soc.* **60**, 2314 (1938).
[2] G. Schwarzenbach, *Helv. Chim. Acta* **33**, 947 (1950).
[3] M. T. Beck and S. Görög, *Chem. Anal.* **48**, 90 (1959).

---

## Synthesis of alkali metal tetrachloroborates*

(*Received* 25 *August* 1959)

In the preparation of alkali metal tetrachloroborates[1] by sealed-tube reaction of boron trichloride and the metal chloride, the high temperatures[2] (400–500°) required resulted in corrosion of the reaction vessel, and the products were contaminated. We have now found that use of a solvent permits preparation of pure $CsBCl_4$ by a relatively simple method.

Nitrobenzene (100 g), cesium chloride (10 g) and boron trichloride (45 g) were charged in a stainless steel-lined pressure vessel and heated to 90° for 3 hr. The reaction product, a slurry, was filtered, and chloroform was added to the filtrate until no further precipitation occurred. The solid was recovered by filtration, washed with chloroform and vacuum dried.

(Found: Cs, 46·5; B, 3·69; Cl, 48·60; C, 0·47. Calc. for $CsBCl_4$: Cs, 46·54; B, 3·79; Cl, 49·67; C, 0). A similar procedure with potassium chloride (15 g) yielded a mixture of KCl and $KBCl_4$ as did the earlier thermal method.[1]

(Found: K, 26·9; B, 4·73; Cl, 68·76. Calc. for $KBCl_4$: K, 20·39; B, 5·64; Cl, 73·97). When lesser amounts of $BCl_3$ were employed, the B:K ratio decreased, which suggests a possible equilibrium situation

$$KCl\,(sln) + C_6H_5NO_2{\cdot}BCl_3 \rightleftarrows KBCl_4\,(sln) + C_6H_5NO_2. \qquad (1)$$

Sodium chloride also dissolved in nitrobenzene as boron trichloride was added; however, addition of chloroform gave a precipitate of sodium chloride.[3] Thallium chloride behaved in an analogous fashion.

These reactions can also be carried out at 30–50° in ordinary glass equipment but products tend to be deficient in $BCl_3$ content. Potassium bromide also dissolved in the $C_6H_5NO_2{\cdot}BB_4$[3] system

* Contribution No. 565 from the Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

[1] E. L. Muetterties, *J. Amer. Chem. Soc.* **79**, 6563 (1957).

[2] This reflects the high lattice energies of the alkali metal chlorides. R. H. Herber *J. Amer. Chem. Soc.* **80**, 5080 (1958)] reported no halogen exchange between RbCl or CsCl (c) and $BCl_3$ (l) at 0° but slow exchange between LiCl and $BCl_3$ at 0°. Since lithium does not appear to form a chloroborate, the exchange mechanism may not involve a chloroborate intermediate. The absence of halogen exchange between CsCl and $BCl_3$ is consistent with the high temperatures required for the formation of $CsBCl_4$ in the absence of a solvent.

[3] Sodium chloride was quantitatively recovered, without even visible alteration of crystallite size, from a NaCl-$BCl_3$ sealed-tube reaction at 500°; E. L. Muetterties.[1]

but chloroform precipitated analytically pure KBr. Perhaps, in the bromine case, an equilibrium analogous to equation (1) exists and lies far to the left.

The chloroborates prepared by the solvent method are much more reactive than those from the thermal method. Atmospheric moisture rapidly effects hydrolysis of these chloroborates. They dissolve in the $C_6H_5NO_2{\cdot}BCl_3$ complex but basic solvents such as amines, nitriles and ethers react irreversibly to form the metal chloride and the $BCl_3$ complex of the base. For example, a slurry of $KBCl_4$ in toluene reacted exothermally with pyridine at 25° to form KCl and a solution from which $BCl_3{\cdot}C_5H_5N$ was isolated.

(Found: B, 5·59; Cl, 53·13; C, 31·18; H, 2·81; N, 6·98; m.p. 111–112°. Calc. for $BCl_3{\cdot}C_5H_5N$: B, 5·51; Cl, 54·19; C, 30·59; H, 2·57; N, 7·14; m.p. 113–114°.) Ethyl ether and $CsBCl_4$ slowly evolved ethyl chloride at 25°.

E. L. Muetterties

*Central Research Department*
*Experimental Station*
*E. I. du Pont de Nemours and Company*
*Wilmington, Delaware*

---

## Thermal decomposition of some oxalates

(*Received* 22 *July* 1959; *in revised form* 3 *September* 1959)

Recently methods have been developed to determine the rate dependent parameters, such as order of reaction and energy of activation, of a chemical reaction from thermogravimetry and differential thermal analysis.[1,2] We report here these parameters for the decomposition of thorium, lanthanum and uranium oxalates, determined by these methods.

Vol. 12 1959/6

### *Experimental*

A "Stanton" high-temperature thermobalance (manufactured by Stanton Instruments Ltd., England) was used for the thermogravimetric measurements. The rate of heating was maintained at 6°C/min. The apparatus for differential thermal analysis was essentially similar to the one described by Gruver,[3] except that the sample holder consisted of a rectangular block of fire brick with two holes capable of holding platinum cells 8 mm dia. and 15 mm in height. The cells were capable of holding 0·7 g of tightly packed alumina. The rate of heating of the platinum wire wound furnace was controlled and recorded by a Honeywell-Brown programme controller recorder. Chromel–alumel thermocouples were employed and the differential temperature was recorded on a differential millivolt recorder. The rate of heating was 6°C/min.

About 500 mg of the sample was taken for each thermogravimetric study. The weight losses were within 2 per cent of the theoretical values. For differential thermal analysis, the sample was well mixed with alumina (E. Merck quality used for chromatographic analysis) and tightly packed in one crucible, whereas in the other, alumina was taken as the reference material.

$Th(C_2O_4)_2 2H_2O$ was prepared by the addition of a hot aqueous solution of thorium nitrate to an excess of hot oxalic acid solution. The precipitated oxalate was filtered, washed with dilute oxalic acid solution and then with water, and dried over sulphuric acid.[4]

$La_2(C_2O_4)_3\ 10H_2O$ was prepared by the method reported by Wendlant[5] and $UO_2C_2O_4\ 3H_2O$ by that reported by Staritzky and Cromer.[6]

[1] E. S. Freemann and B. Caroll, *J. Phys. Chem.* **62**, 394, (1958).
[2] H. J. Brochardt and F. Daniels, *J. Amer. Chem. Soc.* **79**, 41, (1957).
[3] R. M. Gruver, *J. Amer. Ceram. Soc.* **31**, 323, (1948).
[4] *Gmelins Handbuch Der Anorganischen Chemie* No. 44, p. 307. Verlag Chemie GMBH, Bergstr. (1955).
[5] W. Wendlant, *Analyt. Chem.* **30**, 58 (1958).
[6] E. Staritzky and D. T. Cromer, *Analyt. Chem.* **28**, 1363 (1956).

### *Results and Discussion*

*Thorium oxalate.* Fig. 1(A) gives the change in sample weight as a function of temperature. Water of hydration began to come off at 140°C resulting in a horizontal weight level corresponding to the monohydrate. The monohydrate began to decompose at 250°C giving off water to form anhydrous oxalate, which decomposed at 350°C to give $ThO_2$. The decomposition stages agreed well with those of D'Eye and Sellman.[7]

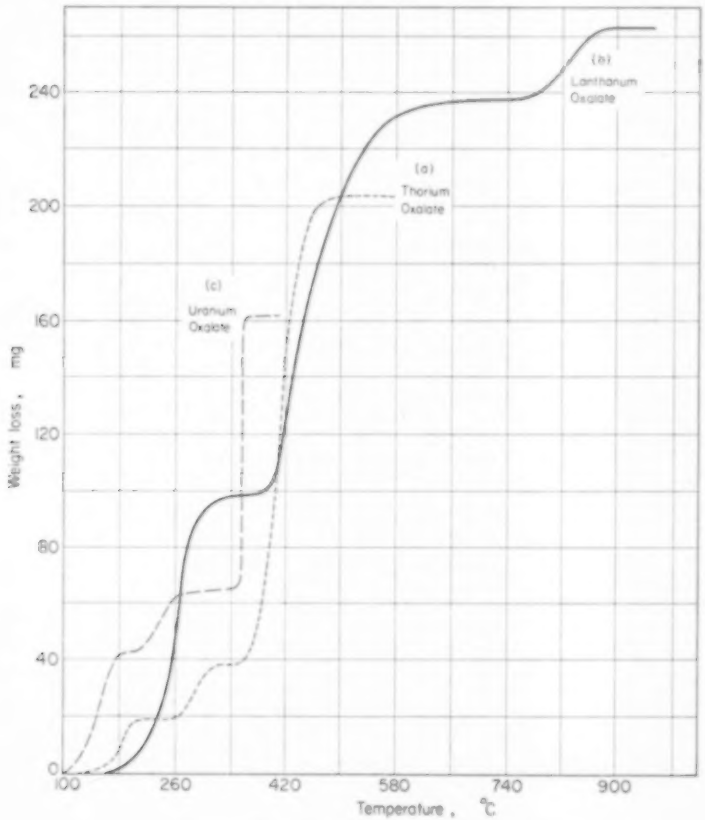



Fig. 1.—Thermograms for the three oxalates.

*Lanthanum oxalate.* Water of hydration began to come off at 170°C, Fig. 1(B), resulting in a horizontal weight level corresponding to $La_2(C_2O_4)_3 2H_2O$. The dihydrate lost water at 390°C followed immediately by the decomposition of oxalate and gave a weight level corresponding to $La_2O_2CO_3$, which decomposed at 770°C to form $La_2O_3$. (The formation of a compound $La_2CO_5$ is reported by Wendlant[5] and Backer and Klassens.[8]) Wendlant[5] reported the loss of $10H_2O$ as the first step in the decomposition of $La_2(C_2O_4)_3 10H_2O$. With the initial weight of about 120 mg as taken by him, the difference in weight loss between $8H_2O$ and $10H_2O$ was about 5 mg as against 20 mg in our case. A horizontal weight level corresponding to $La_2(C_2O_4)_3 2H_2O$ was obtained by us, whereas in his case "the composition approached the anhydrous oxalate at 380°C". As $La_2(C_2O_4)_3 2H_2O$ decomposed directly to "$La_2O_3$, $CO_2$" the anhydrous oxalate could not be weighed for gravimetric purposes. Though the temperatures of decomposition for the latter two steps agreed

[7] R. W. M. D'Eye and P. G. Sellman. *J. Inorg. Nucl. Chem.* **1**, 143 (1955).
[8] H. J. Backer and K. H. Klassens, *Z. Anal. Chem.* **81**, 104 (1930).

in both cases, there was no agreement for the first step. The temperatures of decomposition observed by us agreed well with those obtained by the differential thermal analysis method.

*Uranium oxalate.* The tri-hydrate, Fig. 1(C), lost 2 molecules of water at 100°C, and then lost 1 molecule at 170°C to form the anhydrous oxalate. The decomposition of uranium oxalate was extremely rapid at 350°C. The differential thermal analysis curves for the three oxalates are shown in Fig. 2.

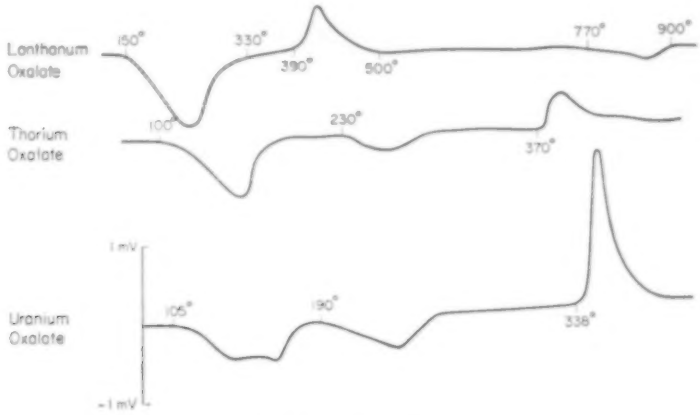



FIG. 2.—DTA curves.

TABLE 1.—DECOMPOSITION OF Th, La AND U OXALATES

| | Temperature of decomposition (°C) | | Energy of activation (kcal/mole) | |
|---|---|---|---|---|
| | Thermo-gravimetry | Differential thermal analysis | Thermo-gravimetry | Differential thermal analysis |
| $Th(C_2O_4)_2 \cdot 2H_2O$ | | | | |
| $Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)H_2O + H_2O$ | 140 | 120 | 26 | 20 |
| $Th(C_2O_4)_2 \cdot H_2O \rightarrow Th(C_2O_4)_2 + H_2O$ | 260 | 230 | 36 | 42 |
| $Th(C_2O_4)_2 \rightarrow ThO_2 + 2CO_2 + 2CO$ | 360 | 370 | 55 | 52 |
| $La_2(C_2O_4)_3 \cdot 10H_2O$ | | | | |
| $La_2(C_2O_4)_3 \cdot 10H_2O \rightarrow La_2(C_2O_4)_3 \cdot H_2O + 8H_2O$ | 160 | 150 | 14 | 17 |
| $La_2(C_2O_4)_3 \cdot 2H_2O \rightarrow La_2O_3CO_2 + 3CO + 2CO_2 + 2H_2O$ | 400 | 390 | .. | .. |
| $La_2O_3CO_2 \rightarrow La_2O_3 + CO_2$ | 760 | 770 | 85 | 85 |
| $UO_2C_2O_4 \cdot 3H_2O$ | | | | |
| $UO_2C_2O_4 \cdot 3H_2O \rightarrow UO_2C_2O_4 \cdot H_2O + 2H_2O$ | 100 | 105 | 19 | 22 |
| $UO_2C_2O_4 \cdot H_2O \rightarrow UO_2C_2O_4 + H_2O$ | 210 | 190 | 31 | 29 |
| $UO_2C_2O_4 \rightarrow$ Uranium oxides $+ CO_2 + CO$ | 365 | 340 | .. | 85 |

Vol. 12 1959/6

*Calculations of the rate parameters.* The order of reaction and energy of activation were calculated from the equations.[1,2]:

$$\frac{-(E/2{\cdot}3R)\,(\Delta T^{-1})}{\Delta \log W_a} = -X + \frac{\Delta \log dW/dt}{\Delta \log W_a}, \qquad \text{(i)}$$

$$K = \Delta T/A - a \qquad \text{(ii)}$$

for the values obtained by the thermogravimeteric and DTA methods respectively. The order of reaction, as determined by thermogravimetry, was found to be between 0·7 and 1·0. Equation (ii) derived for DTA was for a first order reaction in the case of liquids. Here it is extended to solid state decomposition. The ln $k$ vs. $(1/T)$ plot gave a straight line showing that the order of reaction to be one for all decompositions studied. The values of the energy of activation for the various stages of decomposition (Table 1) obtained by the two methods agreed well. As the second step in the decomposition of lanthanum oxalate involved both the loss of water and decomposition of oxalate, no values were calculated. The DTA experiments were also carried out with the rate of heating 10°C/min. The resulting values agreed with those obtained with the rate 6°C/min. As the "Stanton" thermobalance had a fixed rate of heating (6°C/min) equation (i) could not be tested with a different rate of heating.

*Acknowledgements*—The authors wish to thank Dr. J. SHANKAR and Dr. V. T. ATHAVALE for their helpful suggestions.

*Atomic Energy Establishment*
*Trombay, Bombay*

V. M. PADMANABHAN
S. C. SARAIYA
A. K. SUNDARAM

---

## The half-life of americium-243

(*Received* 8 *September* 1959)

AMERICIUM has two beta-stable isotopes, of masses 241 and 243. The former isotope is produced by the beta decay of $^{241}$Pu, a product of all natural uranium reactors, and until quite recently it has been the isotope used in most chemical studies of americium. Its half-life has been determined in this laboratory by HALL and MARKIN[1] by measurements of the specific alpha activity of carefully purified chloride and sulphate samples. Their result is 458·1 ± 0·5 years.

Because of its relatively short half-life, $^{241}$Am is not ideal for chemical studies, since its intense alpha activity produces radiation effects. The much longer lived isotope, $^{243}$Am is preferable, and this isotope, which is produced in a very pure state in plutonium samples irradiated for long periods at high neutron fluxes, should become increasingly available. Its half-life has been quoted as 7950 years[2] and 7600 years.[3] A few milligrams of $^{243}$Am were recently extracted in this laboratory from a highly irradiated plutonium sample, and its half-life was re-determined.

Although a specific activity measurement would have been possible with the quantity of material available, it would have been tedious, and the result would probably have been less accurate than that of HALL and MARKIN, who used much larger quantities. It was therefore decided to compare the half-lives of $^{243}$Am and $^{241}$Am by an isotopic dilution method. This method used only a few micrograms of each nuclide and did not require the highest chemical purity.

The $^{243}$Am had been separated by a series of ion exchange steps, and was free of alpha activity due to other elements. It contained a very small proportion of $^{241}$Am, which was of no consequence, since more $^{241}$Am was added for the determinations. The $^{241}$Am was isotopically pure.

Five mixed solutions, containing $^{241}$Am and $^{243}$Am in different proportions, were prepared in dilute nitric acid. The proportions were chosen to cover the optimum range for both mass spectrometry and alpha pulse analysis—i.e. mass ratios $^{243}$Am/$^{241}$Am in the range 2·5 to 5·5, corresponding

[1] G. R. HALL and T. L. MARKIN, *J. Inorg. Nucl. Chem.* **4**, 137 (1957).
[2] J. C. WALLMAN, P. GRAF and L. GODA, *J. Inorg. Nucl. Chem.* **7**, 199 (1958).
[3] J. P. BUTLER, T. A. EASTWOOD, H. G. JACKSON, T. L. COOLINS, M. E. JONES, F. M. ROURKE and R. P. SCHUMAN, Knolls Atomic Power Laboratory Report, KAPL 1781 (1957).

to activity ratios $^{241}Am/^{243}Am$ in the same range. Samples from each solution were analysed mass spectrometrically, and thin sources from each solution were prepared by vacuum sublimation on polished stainless steel disks for alpha pulse analysis.

The mass spectrometer was a Metropolitan-Vickers type MS. 5 instrument with triple filament ion

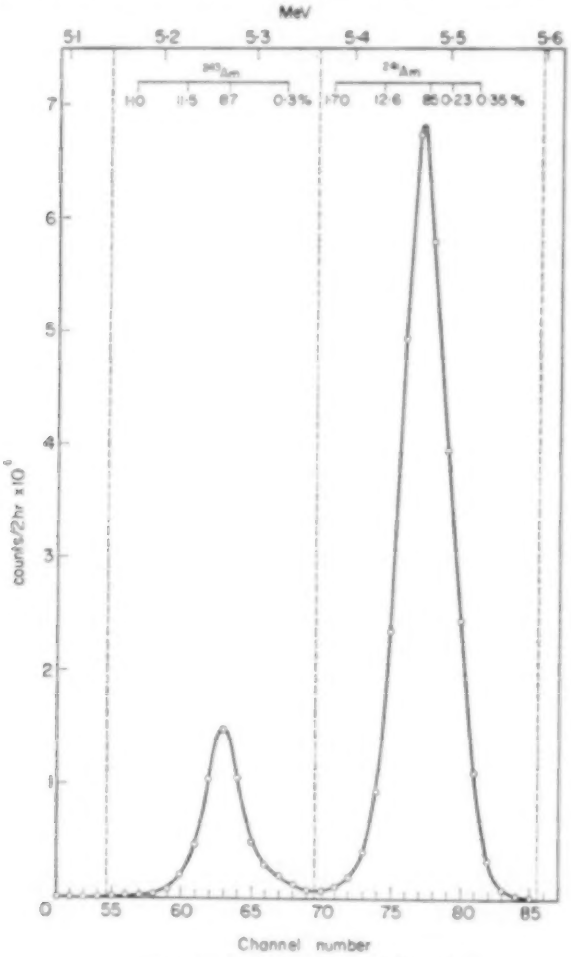



FIG. 1.—Typical pulse analysis result.

source and an electron multiplier collector. The sample placed on one of the side filaments was of the order of $10^{-8}$ g of americium. The results quoted are in most cases the means of 20 scans on a given sample.

The pulse analysis equipment consisted of a gridded ionization chamber, filled with argon containing 10 per cent methane, and connected through conventional amplifiers to a 100 channel pulse analyser (Philips, type 1438B). A typical pulse analysis result is shown in Fig. 1, which also shows the positions and intensities of the main alpha groups of $^{241}Am$[4] and $^{243}Am$.[5] The line of demarcation between the isotopes was drawn at about 5·35 MeV, near the bottom of the valley between the

[4] S. ROSENBLUM, M. VALADARES and J. MILSTED, *J. Phys. Radium* **18**, 609 (1957).

[5] F. ASARO and I. PERLMAN, *Phys. Rev.* **93**, 1423 (1954); F. ASARO, F. S. STEPHENS and I. PERLMAN, unpublished data quoted in *Table of Isotopes*; D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).

Vol. 12 1959/6

two peaks. Normally, the counts in the peaks on either side of this line were simply added, since it was found that estimates of overlap by extrapolation of "tails" did not yield a significantly different result. Each pulse analysis result quoted is a mean of from 6 to 9 observations. The daughter products $^{239}$Pu and $^{237}$Np could not interfere with the determination, since the half-lives involved are long and the alpha pulse analysis was carried out immediately after the ion exchange separation.

If $m$ and $n$ are the atom ratio and activity ratio for $^{243}$Am/$^{241}$Am respectively, then the half-life ratio $^{243}$Am/$^{241}$Am is equal to $m/n$.

The results are quoted in Table 1.

TABLE 1

| Sample | Atom ratio $m$ | Activity ratio $n$ | Half-life ratio $m/n$ |
|---|---|---|---|
| A | 2·623 | 0·1571 | 16·70 |
| B | 5·173 | 0·3115 | 16·61 |
| C | 4·464 | 0·2665 | 16·75 |
| D | 3·125 | 0·1869 | 16·72 |
| E | 3·876 | 0·2315 | 16·74 |

Mean half-life ratio = 16·70.

The very close agreement between four of these results is certainly fortuitous, since both mass spectrometry and pulse analysis results showed standard deviations of about 1 per cent. The standard deviation of the half-life ratio would therefore be about 1·4 per cent. On this assumption, the mean of five observations would be distributed with a standard deviation of $1{\cdot}4/\sqrt{5} = 0{\cdot}63$ per cent; i.e. the ratio is $16{\cdot}70 \pm 0{\cdot}10$.

HALL and MARKIN quote $458{\cdot}1 \pm 0{\cdot}5$ years as the half-life of $^{241}$Am, and if these limits are taken as the standard deviation, and combined with the results of the present work, the half-life of $^{243}$Am may be quoted as $7650 \pm 50$ years. It must be emphasized, however, that the present work has only measured the half-life ratio, and that any future revision of the $^{241}$Am half-life will change this value.

The irradiated plutonium sample was made available through the courtesy of Dr. W. M. MANNING of the Argonne National Laboratory, Lemont, Illinois, with the approval of the U.S. Atomic Energy Commission. We wish to acknowledge this co-operation, and also that of the Phillips Petroleum Company, Arco, Idaho, the British Joint Scientific Mission in Washington, and several colleagues at A.E.R.E., Harwell who co-operated in the transport and chemical processing of the sample.

*Atomic Energy Research Establishment*
*Harwell, Didcot, Berks*

A. B. BEADLE
D. F. DANCE
K. M. GLOVER
J. MILSTEAD

## Synthesis of $^{52}$Mn and $^{74}$As labelled phthalocyanines*

(*Received* 15 *September* 1959)

THE recent availability of $^{52}$Mn and $^{74}$As prompted the investigation of methods for the synthesis of the corresponding metallo phthalocyanines.

Manganous phthalocyanine was prepared by BARRETT and associates[1] by heating *o*-phthalonitrile

* This study was supported by the U.S. Atomic Energy Commission, Contract No. 30-1-2182 and a grant (C 3265) from the National Cancer Institute, National Institutes of Health.

[1] P. A. BARRETT, C. E. DENT and R. P. LINSTEAD, *J. Chem. Soc.* 1719 (1936).

with manganese dioxide. A precursor of uncertain composition was obtained which yielded manganous phthalocyanine on vacuum sublimation. A direct synthesis from the nitrile was desirable in this laboratory. BROOKS *et al.*[2] isolated a precursor from the reaction under oxidizing conditions of *o*-phthalonitrile and cupric salts which gave copper phthalocyanine on pyrolysis or on reduction with alkaline glucose. These observations suggested that a reducing and high boiling solvent should facilitate the reaction. Dimethylformamide is a reducing solvent,[3] but when the nitrile and manganous acetate hydrate were refluxed in this medium negligible product was obtained. However, when a 1, 2-propanediol solution of manganous acetate hydrate was treated with the nitrile and refluxed, manganous phthalocyanine was formed directly.

Arsenic had been introduced into hematoporphyrin by HILL[4] using a saturated solution of arsenic trichloride in pyridine, but the tervalent derivative was unstable in water. Arsenic trichloride however does form a stable ammine containing four ammonia groups. Inspection of an atomic model of a phthalocyanine analogue of porphyrin indicates that the four extra nitrogens are perhaps in close enough proximity to co-ordinate to some extent with a possible arsenic derivative thus conferring additional stability. Chloroaluminium phthalocyanine a similar type compound forms a stable salt in concentrated sulphuric acid.[1] Chloroarsenic phthalocyanine was prepared by a modification of the procedure of BARRETT *et al.*[5] These investigators treated dilithium phthalocyanine with metallic salts in absolute ethanol to obtain metallo phthalocyanines. In this laboratory dimethylformamide was used as the solvent for the reaction between arsenic trichloride and dilithium phthalocyanine. This was particularly advantageous in the labelling procedure as the arsenic trichloride must be obtained from sodium arsenate by treating the latter with concentrated hydrochloric acid under reducing conditions. Dimethylformamide provides a reducing medium and facilitates the reaction by co-ordinating with the arsenic trichloride shifting the equilibrium of the reaction in favour of trichloride formation.

*Experimental*

*Manganous phthalocyanine.* Four molar and one molar proportions of *o*-phthalonitrile and manganous acetate hydrate, respectively were refluxed in 1, 2-propanediol solution until the brown colour was discharged and the solution became greenish black. The mixture was cooled, diluted with water, centrifuged and the black crystals extracted with hot ethanol to remove soluble organic impurities. The compound was obtained in 46 per cent yield and was trace labelled by incorporation of manganous-52 acetate or sulphate into the carrier solution. A pyridine solution had absorption maxima at 340 and 620 mμ which were identical with those of an authentic sample obtained by treating dilithium phthalocyanine with manganous chloride in absolute ethanol.

*Chloroarsenic phthalocyanine.* One molar proportion of dilithium phthalocyanine in dimethylformamide was treated with one molar proportion of anhydrous arsenic trichloride at room temperature. A blue precipitate formed immediately and was collected by centrifugation in 30 min. The crystals were washed with absolute ethanol to remove lithium chloride. A pyridine solution had absorption maxima at 340 and 580 mμ. A silver nitrate test for chloride ion was negative in ethanolic pyridine, but positive after hydrolysis of the compound in hot nitric acid. Solution in concentrated sulphuric acid was accompanied by evolution of hydrogen chloride gas, but prolonged standing was necessary to remove arsenic and the compound was stable to glacial acetic acid. The compound resembles chloroaluminium phthalocyanine in these reactions.

*Chloroarsenic-74 phthalocyanine.* One millicurie (0·5 ml) sodium arsenate was evaporated to dryness with a few drops of concentrated nitric acid, cooled, one drop nitric and several drops concentrated hydrochloric acid added, and the residue warmed in an oil bath at 40° C. Carrier arsenic trichloride (0·1 ml) was added, the temperature of the bath taken to 100° and 2 ml dimethylformamide added followed by 0·5 g dilithium phthalocyanine in the same solvent. The reaction was complete after cooling one hour at room temperature with occasional stirring. The mixture was centrifuged and the solid washed with absolute ethanol until the test for chloride ion and radioactivity was negligible on the washings. Finally the solid was extracted with absolute ether and dried. The compound contained 30 per cent of the arsenic-74 taken in the reaction.

Vol. 12 1959/6

[2] R. A. BROOKS, J. G. BURT, B. F. SKILES and M. S. WHELEN, *J. Org. Chem.* **24**, 383 (1959).
[3] R. T. PFLAUM, A. I. POPOV and N. GOODSPEED, *Analyt. Chem.* **27**, 253 (1955).
[4] R. HILL, *Biochem. J.* **19**, 341 (1925).
[5] P. A. BARRETT, D. A. FRYE and R. P. LINSTEAD, *J. Chem. Soc.* 1157 (1938).

*Summary*

$^{52}$Mn and $^{74}$As labelled phthalocyanines have been prepared by direct synthesis for experimental evaluation. Chloroarsenic phthalocyanine has a stability similar to that of chloroaluminium phthalocyanine. Investigations are in progress on preparation of water soluble derivatives.

*Dept. of Surgery*
*Baltimore City Hospitals*
*Baltimore, Maryland*

H. A. RUTTER, JR.
J. D. MCQUEEN†

† Division of Neurological Surgery, The Johns Hopkins University, School of Medicine, Baltimore, Maryland.

---

## The polarographic behaviour of some square complex compounds of platinum

(*Received* 21 *July* 1959; *in revised form* 3 *October* 1959)

NIKOLYEVA and PRESNYAKOVA[1] showed that during the reduction at the dropping mercury electrode of $K_2Pt(NO_2)_4$ in KCl solution, the peak which occurs in the polarographic curve at an applied potential of −0·5 V, relative to the saturated calomel electrode, changes with time. They suggested that their results might be explained by the formation of such complexes as $K_2Pt(NO_2)_2Cl_2$, $K_2Pt(NO_2)Cl_3$, due to replacement of $NO_2$ groups of the $[Pt(NO_2)_4]$ ion by $Cl^-$ ions. They further pointed out that this method could possibly be used to follow the kinetics of exchange reactions of complex compounds in electrolyte solutions. Their work on the polarographic behaviour of $K_2Pt(NO_2)_4$ in the presence of different supporting electrolytes was repeated and their results were confirmed. In the presence of $NaNO_2$, $KNO_3$ and $Na_2SO_4$ no maxima appeared in the polarographic curves even after the solutions had been standing for 72 hr (Fig. 1). However, when KCl or KBr was used as the supporting electrolyte, a peak developed in the polarographic curve at an applied voltage of −0·5 V and the height of this peak increased with time (Fig. 2).

The polarographic behaviour of $K_2PtCl_4$ in $KNO_2$ as supporting electrolyte was also examined and it was found that the peak in the polarographic curve which occurred at an applied potential of −0·5 V decreased with time (Fig. 3). These phenomena can be explained in terms of the replacement of groups in the complex anion by ions of the supporting electrolyte.

The rate of change of the height of the maximum in the curve was used as a measure of the rate of substitution, the assumption being made that the concentration of the reacting species is proportional to the peak height of the curve. Whether this assumption is justified or not will depend on further experimental evidence. Further, the reaction is undoubtedly complicated by the aquation of the complex ion. As pointed out by STRANKS and WILKINS[2] there are very few unambiguous and authentic examples of direct ligand exchange of transition metal complexes in aqueous solution and it is not known what relative contribution aquation makes to the observed exchange rate.

### *Experimental*

The complex platinum compounds were prepared as described in the literature and their purity confirmed by analysis. The polarographic cell was an H-type cell one arm of which was a saturated calomel electrode. This was separated by a sintered glass disk and an agar plug saturated with potassium chloride from the other arm which contained the solution under test and into which fitted the dropping mercury electrode. A $10^{-3}$ M solution of the complex salt was prepared in the deoxygenated supporting electrolyte. Polarograms were recorded at various intervals of time after the preparation of the solutions.

The polarographic cell was supported in a thermostat at a temperature of 25·0 ± 0·1°C.

[1] N. V. NIKOLYEVA and V. N. PRESNYAKOVA, *Dokl. Akad. Nauk SSSR* **87**, 61 (1952).
[2] D. R. STRANKS and R. G. WILKINS, *Chem. Rev.* **57**, 789 (1957).

*Results and Discussion*

(A) $10^{-3}$ M $K_2Pt(NO_2)_4$ *in* 1 M KCl

The polarogram of $K_2Pt(NO_2)_4$ in KCl immediately after preparation of the solution showed only a slight hump at an applied voltage of −0·5 V, where the current recorded was less than 2 μA.

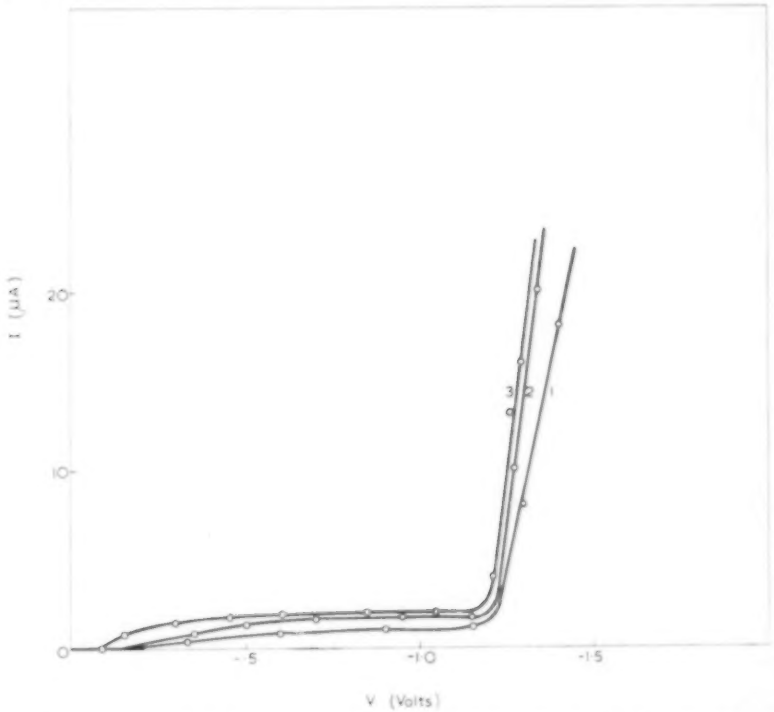



FIG. 1.—$10^{-3}$ M $K_2Pt(NO_2)_4$ in (1) 1 M $NaNO_2$; (2) 1 M $KNO_2$; (3) 1 M $Na_2SO_4$: 72 hr after preparation of the solution.

This hump developed into a prominent peak whose height increased rapidly at first and then more slowly, reaching a maximum value after 24 hr when the peak current was 14·9 μA. The actual values of the peak current at various intervals of time are shown in Fig. 5. The shape of the polarogram after 24 hr was almost identical with that of $K_2Pt(NO_2)_2Cl_2$ in KCl and quite different from that of the other complexes. (Fig. 4). This result suggests that when $10^{-3}$ M $K_2Pt(NO_2)_4$ is reacted with 1 M KCl at 25·0°C, two chloride ions replace two nitro groups from the complex. It would be expected that when $10^{-3}$ M $K_2Pt(NO_2)_3Cl$ is reacted with 1 M KCl, one nitro group would be replaced by a chloride ion. Anomalously, this complex appears to be quite stable in the presence of KCl.

A plot of log $(I_\infty - I_t)$ against $t$, where $I_\infty$ is the final peak current and $I_t$ is the peak current at time $t$, gives a straight line indicating that the reaction is of the first order. The value for the specific rate constant "$k$" was calculated to be $7{\cdot}33 \times 10^{-3}$ $min^{-1}$.

(B) $10^{-3}$ M $K_2PtCl_4$ *in* 1 M $KNO_2$

There is a very marked difference between the polarograms of $K_2PtCl_4$ in $KNO_2$ immediately on preparation of the solution and after it has been standing for 24 hr. Immediately after preparation of the solution there is a prominent peak in the polarogram at an applied potential of −0·5 V, the peak current being 15·2 μA. After the reaction mixture has been standing for 24 hr, the peak has been reduced to a very small hump, the peak current being 1·1 μA. (Fig. 3).

Vol. 12 1959/6

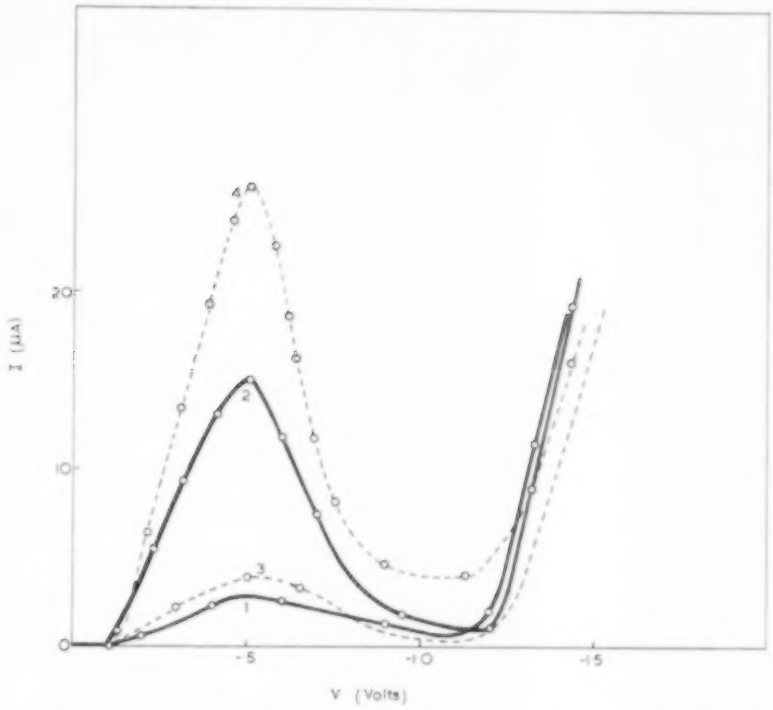



FIG. 2.—$10^{-3}$ M $K_2Pt(NO_2)_4$ in (1) 1 M KCl immediately after preparation of the solution; (2) 1 M KCl 24 hr after preparation of the solution; (3) 1 M KBr immediately after preparation of the solution; (4) 1 M KBr 24 hr after preparation of the solution.

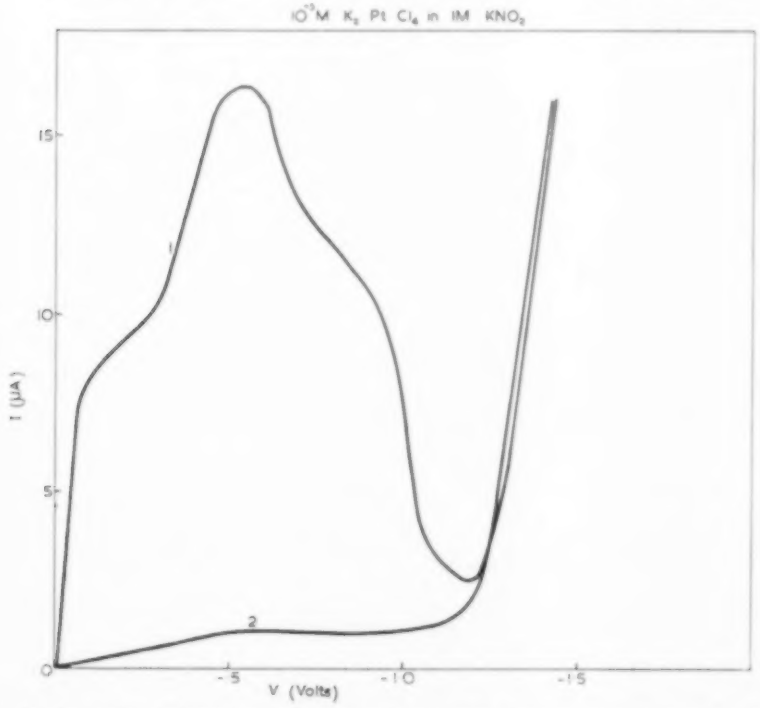



FIG. 3.—$10^{-3}$ M $K_2PtCl_4$ in 1 M $KNO_2$ (1) immediately after preparation of the solution; (2) 24 hr after preparation of the solution.

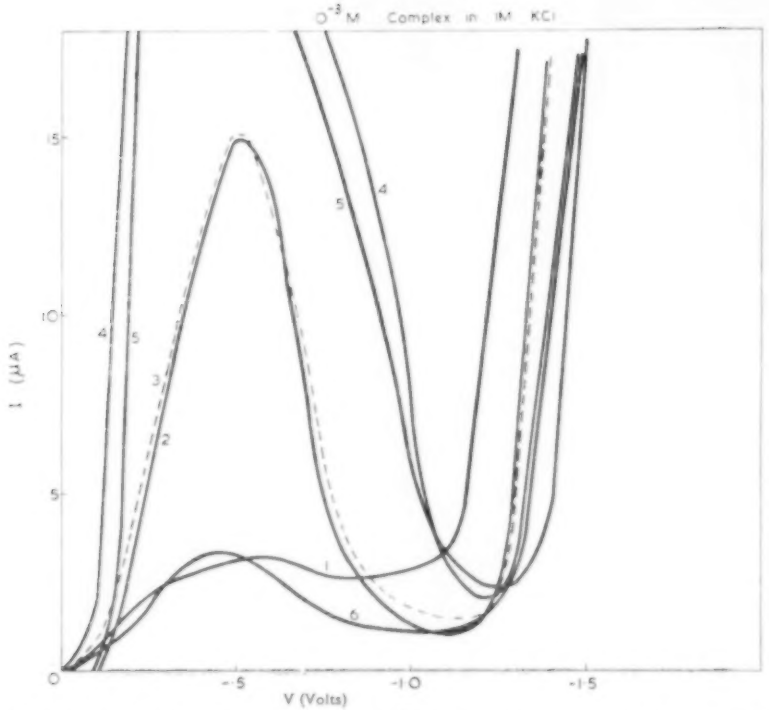



FIG. 4.—Polarograms of complexes ($10^{-3}$ M) in 1 M KCl (1) $K_2Pt(NO_2)_4$—$\frac{1}{4}$ hr after preparation of the solution; (2) $K_2Pt(NO_2)_4$—24 hr after preparation of the solution; (3) $K_2Pt(NO_2)_2Cl_2$—24 hr after preparation of the solution; (4) $K_2PtCl_4$—24 hr after preparation of the solution; (5) $K_2Pt(NO_2)Cl_3$—24 hr after preparation of the solution; (6) $K_2Pt(NO_2)_3Cl$—24 hr after preparation of the solution.

Vol. 12 1959/6

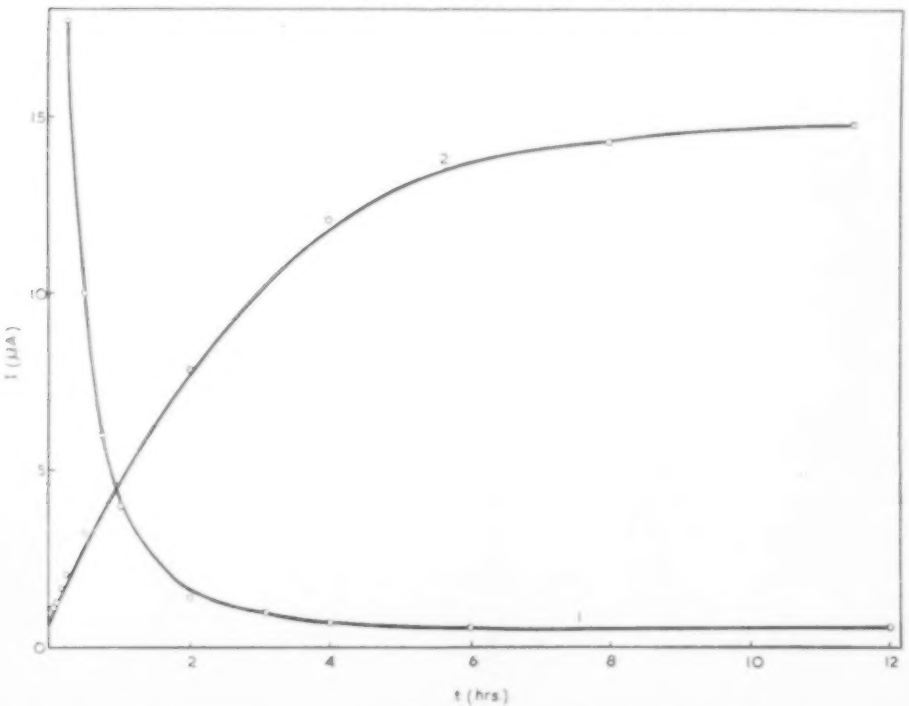



FIG. 5.—Peak current of (1) $10^{-3}$ M $K_2PtCl_4$ in 1 M $KNO_3$; (2) $10^{-3}$ M $K_2Pt(NO_2)_4$ in 1 M KCl; as a function of time.

It is difficult in this case to predict how far the substitution has proceeded because there is not a great deal of difference between the polarograms of $K_2Pt(NO_2)_4$ in 1 M $KNO_2$ and of $K_2Pt(NO_2)_2Cl_2$ in 1 M $KNO_2$.

Fig. 5 shows the change in the peak current with time at an applied voltage of −0·5 V for the complex $10^{-3}$ M $K_2PtCl_4$ in 1 M $KNO_2$.

G. CURTHOYS
J. H. GREEN

*Dept. of Science, Newcastle University College*
*University of New South Wales*
*Tighe's Hill, 2N, New South Wales*
*Australia*

---

## Exchange properties of ammonium salts of 12-heteropolyacids. Sorption of caesium on ammonium phosphotungstate and phosphomolybdate

(*Received* 8 *October* 1959)

THE exchange properties of ammonium phosphomolybdate were suggested by BAXTER and GRIFFIN,[1] and later by THISTLETHWAITE[2]. BUCHWALD and THISTLETHWAITE[3] described the sorption of potassium, rubidium, caesium, thallium and alkaline earths on ammonium phosphomolybdate as being due to isomorphous exchange of an ion in the lattice; the sorbing cation was assumed to be able to replace both ammonium and hydrogen ions present in a molecule of ammonium phosphomolybdate. The exchange properties of ammonium phosphomolybdate were used by SMIT[4] for the column separation of $^{24}Na$, $^{42}K$, $^{86}Rb$ and $^{134}Cs$, using ammonium nitrate solution in various concentrations as eluant. The determination of radioactive caesium in dilute solutions by sorption on thallium phosphomolybdate has also been described.[5]

Our earlier studies on the reaction between alkali metals and heteropolyacids indicated the instability of phosphomolybdic acid and its salts in solutions under certain conditions. On the other hand phosphotungstic acid resists hydrolysis and is stable even in strong acid media. This paper describes the exchange properties both of ammonium phosphotungstate and ammonium phosphomolybdate.

### *Experimental*

Ammonium phosphotungstate and ammonium phosphomolybdate were prepared by precipitation of commercial 12-heteropolyacids with excess of $NH_4Cl$ in 0·1 N HCl; they were washed with 0·1 N HCl, then absolute alcohol, and dried at 40–60° C. In the dry product $NH_4$ was determined by Nessler's colorimetric method, W and Mo gravimetrically with oxine or colorimetrically with rhodanide, and water by ignition to constant weight at 450° C. Phosphorus was determined colorimetrically as phosphotungstovanadic acid or phosphomolybdovanadic acid. The analyses correspond to the formulae

$(NH_4)_{2\cdot67}H_{0\cdot33}(P\,W_{12}O_{40}).9{\cdot}8\,H_2O$, abbreviated to $NH_4PW$

$(NH_4)_{2\cdot95}H_{0\cdot05}(P\,Mo_{12}O_{40}).11{\cdot}6\,H_2O$ abbreviated to $NH_4PMo$.

(a) The prepared salts (0·1 g) were added to 2 ml of HCl or $HNO_3$ (0·2–10 N) and after reaching equilibrium solid and liquid phase were analysed (Tables 1 and 2).
Whereas in the solid phase of $NH_4PW$ the replacement of ammonium ions by hydrogen increases continuously, the calculated values of the ratio $NH_4/P$ for $NH_4PMo$ are irregular, due to decomposition of $NH_4PMo$ by the acid.

[1] G. P. BAXTER and R. C. GRIFFIN, *Amer. Chem. J.* **34,** 204 (1905).
[2] W. P. THISTLETHWAITE, *Analyst.* **72,** 531 (1947).
[3] H. BUCHWALD and W. P. THISTLETHWAITE, *J. Inorg. Nucl. Chem.* **5,** 341 (1958).
[4] J. VAN R. SMIT, *Nature, Lond.* **181,** 1530 (1958).
[5] HARA TADASHI, *Bull. Chem. Soc. Japan* **31,** 635 (1958).

TABLE 1.—EQUILIBRIUM IN THE SYSTEM: AMMONIUM PHOSPHOTUNGSTATE–HYDROCHLORIC ACID, AMMONIUM PHOSPHOTUNGSTATE–NITRIC ACID

| Acid concentration N | | Moles of $NH_4$* | | g atoms of P* | | g atoms of W* | | $NH_4$/P moles solid phase |
|---|---|---|---|---|---|---|---|---|
| | | Liquid phase | Solid phase | Liquid phase | Solid phase | Liquid phase | Solid phase | |
| 0·2 | HCl | 11·6 | 88·4 | Was not | 37·5 | 0·25 | 449·75 | 2·36 |
| | $HNO_3$ | 9·8 | 90·2 | found | 37·5 | 0·2 | 449·80 | 2·41 |
| 1·0 | HCl | 18·2 | 81·8 | Was not | 37·5 | 0·3 | 449·70 | 2·18 |
| | $HNO_3$ | 17·0 | 83·0 | found | 37·5 | 0·2 | 449·80 | 2·22 |
| 3·0 | HCl | 22·7 | 77·3 | Was not | 37·5 | 0·25 | 449·75 | 2·05 |
| | $HNO_3$ | 24·8 | 75·2 | found | 37·5 | 0·2 | 449·80 | 2·0 |
| 6·0 | HCl | 24·8 | 75·2 | Was not | 37·5 | 0·2 | 449·80 | 2·0 |
| | $HNO_3$ | 25·4 | 74·6 | found | 37·5 | 0·2 | 449·80 | 1·98 |
| 10·0 | HCl | 27·0 | 73·0 | Was not | 37·5 | 0·30 | 449·70 | 1·95 |
| | $HNO_3$ | 26·4 | 73·6 | found | 37·5 | 0·2 | 449·80 | 1·96 |

* Results calculated relative to 100 moles of ammonium in original material.

TABLE 2.—EQUILIBRIUM IN THE SYSTEM: AMMONIUM PHOSPHOMOLYBDATE–HYDROCHLORIC ACID, AMMONIUM PHOSPHOMOLYBDATE–NITRIC ACID

| Acid concentration N | | Moles of $NH_4$* | | g atoms of P* | | g atoms of Mo* | | $NH_4$/P moles solid phase |
|---|---|---|---|---|---|---|---|---|
| | | Liquid phase | Solid phase | Liquid phase | Solid phase | Liquid phase | Solid phase | |
| 0·2 | HCl | 8·5 | 91·5 | 4·06 | 29·27 | 2·95 | 397·05 | 3·13 |
| | $HNO_3$ | 9·5 | 90·5 | 3·97 | 29·36 | 2·33 | 397·67 | 3·08 |
| 1·0 | HCl | 17·1 | 82·9 | 5·39 | 27·94 | 18·75 | 381·25 | 2·98 |
| | $HNO_3$ | 18·0 | 82·0 | 6·06 | 27·27 | 20·6 | 374·4 | 3·0 |
| 3·0 | HCl | 21·0 | 79·0 | 4·6 | 28·73 | 22·7 | 377·3 | 2·27 |
| | $HNO_3$ | 23·5 | 76·5 | 5·26 | 28·07 | 43·8 | 356·2 | 2·82 |
| 6·0 | HCl | — | — | — | — | — | — | —† |
| | $HNO_3$ | 23·0 | 77·0 | 6·82 | 26·51 | 24·8 | 375·2 | 2·90 |
| 10·0 | HCl | — | — | — | — | — | — | —† |
| | $HNO_3$ | 17·1 | 82·9 | 9·68 | 23·65 | 6·56 | 393·44 | 3·50 |

* Results calculated relative to 100 moles of ammonium in original material.
† Under these conditions $NH_4PMo$ decomposes strongly.

Vol. 12 1959/6

(b) In caesium phosphotungstate (CsPW) and phosphomolybdate (CsPMo), the exchange between Cs ions and H ions was investigated in a similar way (3 atoms of Cs were originally present in 1 molecule of the heteropolysalt. The content of Cs in the solid phase decreased with increasing acidity of the medium. CsPW does not decompose; the CsPMo decomposes in 8–10 N HCl.

(c) The exchange between Cs and $NH_4$ in $NH_4PMo$ and $NH_4PW$ was examined by shaking 0·1 g of precipitate of $NH_4PW$ or $NH_4PMo$ with 2 ml HCl of varying concentration containing excess 3M Cs labelled with $^{137}Cs$. The precipitate was washed with acid and analysed; Cs was determined radiometrically using an end-window counter. The results are shown in Tables 3 and 4.

TABLE 3.—EQUILIBRIUM IN THE SYSTEM: AMMONIUM PHOSPHOTUNGSTATE–CAESIUM CHLORIDE–HYDROCHLORIC ACID

| HCl concentration N | Cs/P moles solid phase | $NH_4$/P moles solid phase | Cs/$NH_4$ moles solid phase |
|---|---|---|---|
| $H_2O$ | 1·73 | 0·99 | 1·75 |
| 0·01 | 1·72 | 1·05 | 1·64 |
| 0·1 | 1·64 | 0·95 | 1·73 |
| 0·9 | 1·51 | 0·89 | 1·70 |
| 3·0 | 1·58 | 0·86 | 1·84 |
| 5·2 | 1·49 | 0·83 | 1·80 |

TABLE 4.—EQUILIBRIUM IN THE SYSTEM: AMMONIUM PHOSPHOMOLYBDATE–CAESIUM CHLORIDE–HYDROCHLORIC ACID

| HCl concentration N | Cs/P moles solid phase | $NH_4$/P moles solid phase | Cs/$NH_4$ moles solid phase |
|---|---|---|---|
| $H_2O$ | 1·29 | 1·59 | 0·81 |
| 0·01 | 1·22 | 1·41 | 0·87 |
| 0·1 | 1·24 | 1·56 | 0·79 |
| 0·9 | 1·16 | 1·43 | 0·81 |
| 3·0 | 1·15 | 1·39 | 0·83 |
| 5·2 | 1·12 | 1·28 | 0·87 |

The Cs/$NH_4$ ratio in $CsNH_4PMo$ (0·79–0·87), which is also given approximately by BUCHWALD and THISTLETHWAITE,[3] is lower than that in $CsNH_4PW$ (1·64–1·84) under similar conditions. The sorption capacity of $NH_4PW$ is thus higher, whether expressed in moles or by weight.

*Conclusion*

The results indicate quantitatively that ammonium phosphomolydate and ammonium phosphotungstate are able to exchange part of their ammonium for caesium. Equilibrium is attained between ammonium, alkali and hydrogen ions. Ammonium phosphotungstate is stable in neutral and strong acid media and Cs sorption may be influenced over a wide range by the concentrations of both ammonium and hydrogen ions. On the contrary the stability of ammonium phosphomolybdate is lower, and the sorption capacity of ammonium phosphotungstate for caesium is higher than that of ammonium phosphomolybdate. Detailed data will be published later.

J. KRTIL
V. KOUŘIM

*Institute of Nuclear Research*
*Czechoslovak Academy of Sciences*
*Prague*

## Coprecipitation of carrier-free caesium with 12-heteropolyacids in a strong acid medium

(*Received* 8 *October* 1959)

HETEROPOLYACIDS are known to be isomorphous with their alkali salts. If a free heteropolyacid is precipitated from a strong acid medium, even small amounts of alkali present are coprecipitated and enter the crystal lattice. The rate of coprecipitation depends upon the acidity of medium and on the acid; until now this effect has been known only qualitatively and incompletely. In this study the solubility of some saturated diheteropolyacids was determined in strong mineral acids at various concentrations, and the coprecipitation of carrier-free caesium with these acids and with more complex heteropolyacids (triheteropolyacids) was studied

### *Experimental*

The heteropolyacids were obtained either by purification of commercial products or by synthesis [1–5] Analysis of products was carried out by means of standard methods[1–5] or by colorimetry,[6] estimating the coloured heteropolycompounds formed under defined conditions. The following acids were used (calculated from the analytical data):

(1) $H_3(PW_{12}O_{40})\cdot 22H_2O$, abbreviated to **HPW**
(2) $H_3(PMo_{12}O_{40})\cdot 12H_2O$, abbreviated to **HPMo**
(3) $H_4(SiW_{12}O_{40})\cdot 23H_2O$, abbreviated to **HSiW**
(4) $H_4(SiMo_{12}O_{40})\cdot 23H_2O$, abbreviated to **HSiMo**
(5) $H_3(PW_{10}V_2O_{39})\cdot 31H_2O$, abbreviated to **HPWV**
(6) $H_3(PMo_{10}V_2O_{39})\cdot 19H_2O$, abbreviated to **HPMoV**
(7) $H_4(SiW_{10}V_2O_{39})\cdot 30H_2O$, abbreviated to **HSiWV**
(8) $H_4(SiMo_{10}V_2O_{39})\cdot 29H_2O$, abbreviated to **HSiMoV**
(9) $H_3(AsW_{10}V_2O_{39})\cdot 30H_2O$, abbreviated to **HAsWV**
(10) $H_3(AsMo_{10}V_2O_{39})\cdot 19H_2O$, abbreviated to **HAsMoV**
(11) $H_4(SeW_{10}V_2O_{39})\cdot 32H_2O$, abbreviated to **HSeWV**
(12) $H_4(GeW_{10}V_2O_{39})\cdot 26H_2O$, abbreviated to **HGeWV**
(13) $H_5(BW_{10}V_2O_{39})\cdot 21H_2O$, abbreviated to **HBWV**

*Solubility*

Weighed amounts of the heteropolyacids (1)–(4) (0·01–3·0 g) were mixed with 0·1–14·0 N $HNO_3$, HCl, $H_2SO_4$ or $HClO_4$ (1–5 ml). Equilibrium was attained by stirring at 20 ± 0·1°C for 2–12 hr, and in the case of HPMo for 10 min. The resulting concentrations of mineral acid were corrected for the dissolved crystal water. After centrifuging, the pipetted and weighed samples of supernatant were evaporated, ignited at 450–500°C to defined compounds, and weighed.

*Coprecipitation*

To weighed amounts of the heteropolyacids (1)–(8) (10–50 mg) was added 0·03 ml of $^{137}$CsCl solution (<20 $\mu$g of salts/ml, 20 $\mu$C $^{137}$Cs/ml), in which the heteropolyacid dissolved, and the solution was then precipitated with 0·33 ml of ~12 N HCl, $HNO_3$, $H_2SO_4$ or $HClO_4$; the acids (9)–(13) were precipitated only with $HNO_3$. The precipitate was centrifuged after several minutes and the activity of the supernatant samples was measured with an end-window G.M. counter.

### *Results*

*Solubility* (Fig. 1)

The solubility of HPW in water expressed as the anhydrous compound $H_3(PW_{12}O_{40})$ was found to be 173·6 g/100 ml of solution; the density of the solution (d) was found to be 2·475. Similarly for

HPMo 93·4 g/100 ml, $d = 1{\cdot}731$
HSiMo 153·3 g/100 ml, $d = 2{\cdot}180$
HSiW 222·3 g/100 ml, $d = 2{\cdot}922$.

(1) E. A. NIKITINA, *Zh. Obshch. Khim.* **8**, 751 (1938).
(2) A. I. KOKORIN, *Zh. Obshch. Khim.* **24**, 966 (1954); **24**, 971 (1954).
(3) A. I. KOKORIN and N. A. POLOTEBNOVA, *Zh. Obshch. Khim.* **24**, 1137 (1954); **24**, 1718 (1954).
(4) N. A. POLOTEBNOVA, *Ucenie Zapiski Kishinev. Univ.* **27**, 83 (1957).
(5) A. I. KOKORIN and M. S. SCELKUNOVA, Private communication.
(6) V. KOUŘIM and J. KRTIL, To be published.

Vol. 12 1959/6

These values are in accordance with the data of other authors.[7–12] Till now the decrease in solubility of heteropolyacids in acid media has not been measured except for HPW.[12]

The heteropolyacids HPW, HSiW and HSiMo are stable in concentrated acids, HPMo decomposes in HCl, $H_2SO_4$ and $HClO_4$ above 4–6N and in $HNO_3$ above 8N. The relatively small

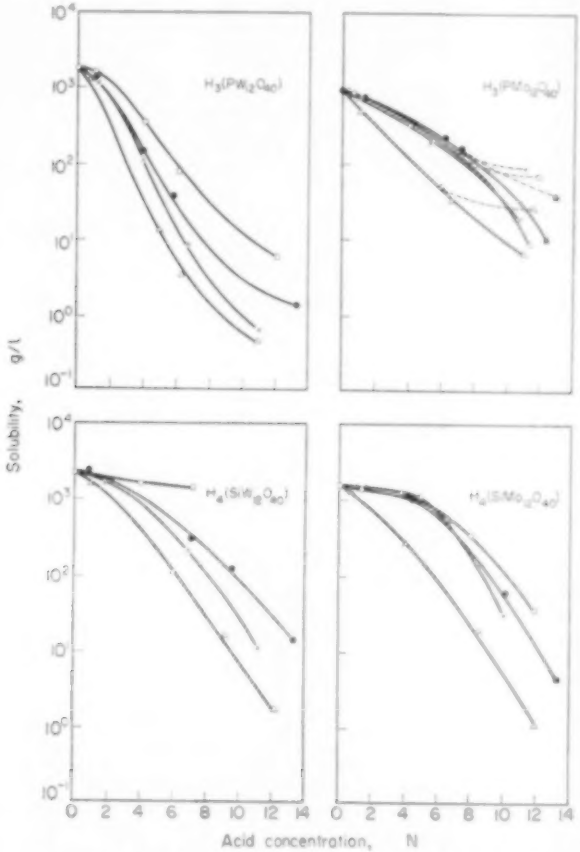



FIG. 1.—Solubility of heteropolyacids in mineral acids.
○ $HNO_3$ ● $H_2SO_4$
× HCl △ $HClO_4$
Full lines for $H_3(PMo_{12}O_{40})$—equilibrium after 10 min.
Broken lines—decomposition of heteropolyacid.

influence of $HNO_3$ on the solubility of HSiW is interesting. The mutual action of heteropolyacids and strong mineral acids does not eliminate the possibility of formation of complicated complexes.

*Coprecipitation*

The degree of coprecipitation of carrier-free caesium with free heteropolyacids increases with increasing amount of the heteropolyacid. To attain maximum yields with our experimental procedure, 50 mg of heteropolyacid was sufficient in most cases. It is necessary to note that the volume

[7] C. MARIGNAC, *Ann. Chim. Phys.* **3**, 15 (1864).
[8] H. COPAUX, *Ann. Chim. Phys.* **7**, 127 (1906).
[9] A. V. RAKOVSKII and E. A. NIKITINA, *Zh. Obshch. Khim.* **6**, 50 (1936).
[10] E. A. NIKITINA and O. N. SOKOLOVA, *Zh. Neorg. Khim.* **2**, 2231 (1957).
[11] A. K. BABKO and JU. F. SKARAVSKII, *Khim. i Khim. Technol.* **2**, 157 (1959).
[12] V. I. SPICYN and P. JA. MATJAZ, *Zh. Neorg. Khim.* **4**, 830 (1959).

of precipitate does not always correspond to the amount of caesium captured, especially for precipitates produced in $HClO_4$. The best results with diheteropolyacids (1)–(4) were obtained with acids having a central P atom together with $HNO_3$ and similarly Si with HCl, the worst results were obtained with the combinations of P with $HClO_4$, and of Si with $HClO_4$ or $HNO_3$. Triheteropolyacids (5)–(13) generally give lower results than corresponding diacids. (Table 1.)

TABLE 1.—COPRECIPITATION OF CARRIER-FREE CAESIUM

| Heteropolyacid | Coprecipitated Cs (%) acid concentration ~ 12 N | | | |
|---|---|---|---|---|
| | $HNO_3$ | HCl | $H_2SO_4$ | $HClO_4$ |
| HPW | 99·5 | 99·4 | 99·2 | 91·8 |
| HPMo | 99·0 | 97·7 | 98·8 | 97·8 |
| HSiW | — | 97·4 | 92·0 | 77·0 |
| HSiMo | 80·0 | 97·0 | 98·2 | 78·0 |
| HPWV | — | 77·0 | 50·0 | 86·0 |
| HPMoV | 97·0 | 80·0 | 73·0 | 83·0 |
| HSiWV | — | — | — | 62·0 |
| HSiMoV | 33·0 | 83·0 | 40·0 | 36·0 |
| HAsWV | 21·0 | — | — | — |
| HAsMoV | 88·0 | — | — | — |
| HSeWV | 49·0 | — | — | — |
| HGeWV | 5·0 | — | — | — |
| HBWV | 6·0 | — | — | — |

*Note.* Detailed data, including the discussion, will be published later.

*Institute of Nuclear Research*
*Czechoslovak Academy of Sciences*
*Prague*

V. KOUŘÍM

Vol. 12 1959/6

## Synthesis of methyldichlorophosphine and dimethylchlorophosphine*

(*Received* 15 *October* 1959)

METHYLDICHLOROPHOSPHINE (II) has been mentioned in numerous publications[1] but the only reference to its synthesis is a footnote stating that it "was prepared by the reduction of the complex $(CH_3PCl_3)(AlCl_4)$ (I) in acetonitrile with aluminium".[2] A more convenient laboratory synthesis is the reduction of the complex (I), prepared from methyl chloride, phosphorus trichloride and aluminium chloride,[3] with phenyldichlorophosphine in the presence of phosphorus oxychloride.

$$\underset{\text{I}}{(CH_3PCl_3)(AlCl_4)} + \phi PCl_2 + POCl_3 \rightarrow \underset{\text{II}}{CH_3PCl_2} + \phi PCl_4 + AlCl_3{\cdot}POCl_3$$

Tributylphosphine is also a satisfactory reducing agent but gives a somewhat lower yield.

* Contribution No. 570 from the Central Research Dept., Experimental Station E. I. du Pont de Nemours and Company, Wilmington, Deleware.

[1a] L. Z. SOBOROVSKII and YU. M. ZINOV'EV, *Zh. Obshch. Khim.* **24**, 516 (1954); [b] L. D. QUIN and C. H ROLSTON, *J. Org. Chem.* **23**, 1693 (1958).
[2] F. W. HOFFMANN and T. R. MOORE, *J. Amer. Chem. Soc.* **80**, 1150 (1958).
[3] J. P. CLAY, *J. Org. Chem.* **16**, 892 (1951).

Dimethylchlorophosphine (IV) was prepared for the first time recently by cleavage of dimethylaminodimethylphosphine with hydrogen chloride.[4] Tetramethyldiphosphine disulphide (III), obtainable in 85 per cent yield from methylmagnesium bromide and thiophosphoryl chloride,[5] has now been converted to dimethylchlorophosphine in 46 per cent yield by simultaneous reduction and cleavage with phenyldichlorophosphine.

$$\underset{\underset{\underset{\text{III}}{\text{S}\quad\text{S}}}{\|\quad\|}}{(CH_3)_2P{-}P(CH_3)_2} + \phi PCl_2 \rightarrow \underset{\text{IV}}{2(CH_3)_2PCl} + (\phi PS)$$

*Experimental*

*Methyldichlorophosphine.* The complex (I) prepared by shaking 12 g of methyl chloride, 31 g of phosphorus trichloride and 29 g of aluminium chloride in a sealed glass tube[3] was placed in a 200 ml flask connected to a 6 in. Vigreaux column. Addition of 21 ml of phosphorus oxychloride produced an exothermic reaction and most of the complex dissolved. Phenyldichlorophosphine (31 ml) was added and the mixture was heated to 130°. At that temperature the mixture became homogeneous and 23 ml of a clear, colorless liquid distilled at 80–98°. Redistillation in a nitrogen atmosphere gave 21 g (82 per cent) of methyldichlorophosphine, b.p. 80–84°. The infra-red spectrum was identical to that of an authentic sample supplied by the U.S. Army Chemical Corps and contained a strong band for the methyl group at 7·75 $\mu$, as reported by Cason and Baxter.[6] The $^{31}P$ magnetic resonance was a sharp peak at −191 p.p.m., relative to 85 per cent phosphoric acid (literature value[7] −191·2 p.p.m.).

Substitution of tributylphosphine for the phenyldichlorophosphine used in this experiment gave methyldichlorophosphine in only 61 per cent yield.

*Dimethylchlorophosphine.* A mixture of 9·3 g of tetramethyldiphosphine disulphide and 20·3 ml of phenyldichlorophosphine was heated in a nitrogen atmosphere until the mixture became homogeneous at about 200°. The clear, yellow solution was distilled to give 6·8 ml of a clear, colorless liquid b.p. 62–70°. Redistillation gave 4·2 g (46 per cent) of clear, colorless dimethylchlorophosphine, b.p. 77°, m.p. −4 to 0° (literature values:[4] b.p. 73°, m.p. −1·4 to −1·0°). The infra-red spectrum contained bands assignable to saturated CH bonds at 3·35 $\mu$ and to a methyl group at 7·75 $\mu$. The proton magnetic resonance contained a symmetrical doublet in the methyl region. The $^{31}P$ magnetic resonance was a single, sharp peak with a chemical shift of −93·0 p.p.m., relative to 85 per cent phosphoric acid. The mass spectrum contained major peaks at 81, 83, 96 and 98 units in the proper ratio for the presence of one chlorine atom in the molecule.

*Central Research Department Experimental Station* G. W. Parshall
*E. I. du Pont de Nemours and Company*
*Wilmington, Delaware*

[4] A. B. Burg and P. J. Slota, *J. Amer. Chem. Soc.* **80**, 1107 (1958).
[5] H. Reinhardt, D. Bianchi and D. Mölle, *Ber.* 90, 1657 (1957).
[6] J. Cason and W. N. Baxter, *J. Org. Chem.* **23**, 1303 (1958).
[7] N. Muller, P. C. Lauterbur and J. Goldenson, *J. Amer. Chem. Soc.* **78**, 3557 (1956).

ol. 12 9/60

## A source of error in the determination of uranium-235 by gamma-spectrometry

(*Received* 14 *September*, 1959; *in revised form* 15 *October* 1959)

Uranium-235 emits $\gamma$-rays at 184 keV which can easily be resolved from other $\gamma$-rays emitted by uranium by using a scintillation spectrometer; data on radiation emitted by uranium and its daughters are given in the Table 1.

A number of workers have measured the intensity of $\gamma$-rays in an energy band at 184 keV to determine $^{235}U$ concentrations in uranic samples.

TABLE 1.—PRINCIPAL RADIATIONS FROM URANIUM AND ITS SHORT-LIVED DAUGHTERS[1,2]

| Isotope | Type of decay | Half-life | Principal particle energies (MeV) and occurrence percentages | Principal $\gamma$-energies (MeV) and % $\gamma$/disintegration |
|---|---|---|---|---|
| $^{238}U$ | $\alpha$ | $4{\cdot}5 \times 10^9$ years | 4·182 (77%), 4·134 (23%) | 0·045 mostly internally converted |
| $^{234}Th$ | $\beta$ | 24·1 days | 0·100 (35%), 0·191 (65%) | 0·029, 0·0628 ($e_L/\gamma = 0{\cdot}45$), 0·0914 ($e_L/\gamma = 2{\cdot}0$) |
| $^{234m}Pa$ ($UX_2$) | $\beta$ | 1·175 months | 0·58 (1%), 1·50 (9%) 2·31 (90%) | 0·043, 0·230, 0·255, 0·770, 0·803, 1·01, 1·24, 1·44, 1·69, 1·83 (< 1%) |
| $^{235}U$ | $\alpha$ | $7{\cdot}13 \times 10^8$ years | 4·58 (10%), 4·40 (83%) | 0·110 (5%), 0·146 (12%), 0·184 (55%), 0·209 (<4%) |
| $^{231}Th$ | $\beta$ | 26·5 hr | 0·134 (20%), 0·218 (33%) | 0·022 (13%), 0·085 (7%), 0·122 (0·1%), 0·167 (0·1%), 0·208 (0·02%) |
| $^{234}U$ | $\alpha$ | $2{\cdot}47 \times 10^5$ years | 4·768 (72%), 4·71 (28%) | 0·118 (<0·3%) |

*Note:* $e/\gamma$ = ratio of conversion electrons to $\gamma$ quanta emitted.

Such measurements at low $^{235}U$ abundances have been made by MORRISON and COSGROVE[3], who estimated the intensity of the 184 keV line from $^{235}U$ from a spectrum, and by MILLER,[4] MEYER,[5] REYNOLDS and ELDRIDGE[6] and JACOB,[7] who measured the total radiation at 184 keV with a single-channel analyser.

While some of these workers concluded that part of the radiation at 184 keV was attributable to $^{234}Pa$ (a daughter of $^{238}U$) and used techniques to overcome errors caused by it, it does not appear to have been appreciated that the background radiation is the result of bremsstrahlung emitted by $\beta$-rays from $^{234}Pa$.

It has been calculated, for the case of a thick natural uranium metal source in which the daughters are in equilibrium, that the intensity of bremsstrahlung at 184 keV is of the same order as the intensity from the $\gamma$-rays produced by $^{235}U$.

The work described here confirms this prediction and examines some of the factors which influence this background.

### *Experimental Determination of the Origin of the Background Gamma Radiation at* 184 keV

#### *Apparatus*

A conventional scintillation gamma spectrometer was used for the measurements. This consisted of a NaI (Tl) crystal, 1 in. thick and 1½ in. dia., mounted directly on an E.M.I. type 6097F photomultiplier. Pulses from the multiplier were amplified by a standard linear amplifier and fed to a single-channel pulse analyser. Two scaling units coupled in series were used to count pulses from the analyser. Samples were rigidly mounted on top of the crystal. To remove the effect of the 2·3 MeV $\beta$-ray from $^{234}Pa$, a $\beta$-filter of Perspex was inserted between the sample and the crystal.


[1] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* **30**, 585 (1958).
[2] V. S. DZELEPOV and L. K. PEKER, Atomic Energy of Canada Ltd., AECL-457 (1957).
[3] G. H. MORRISON and J. F. COSGROVE, *Analyt. Chem.* **29**, 1770 (1957).
[4] D. G. MILLER, General Electric Co., HW-39969 (1955).
[5] R. C. MEYER, NBL 127. U.S.A.E.C. Research and Development Progress Report for the Period July 1955 to December 1955 (1956).
[6] S. A. REYNOLDS and J. S. ELDRIDGE, Oak Ridge National Laboratory, CF-57-1-3 (1957).
[7] M. E. JACOBS, Goodyear Atomic Corporation, GAT-254 (1958).


Vol. 12 1959/6

*Radiation from uranium rods—variation with concentration*

A typical spectrum of the low-energy gamma radiation from a 1 in. thick uranium metal rod, in which the daughter activity is in equilibrium, is shown in Fig. 1. There is a complex peak at 90–100 keV, caused mainly by $^{234}$Th and uranium X-radiation. There is apparently a continuous background under the $^{235}$U gamma line at 184 keV. (The counter background has been subtracted in all curves

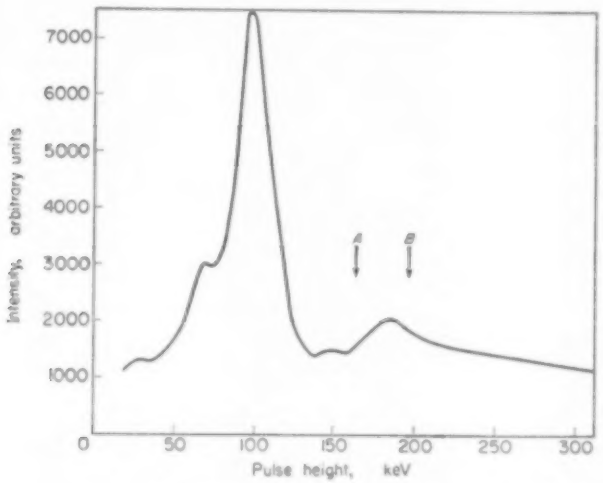



FIG. 1.—Gamma spectrum of natural uranium metal ¼ in. thick.

shown.) It was shown that the magnitude of this background was independent of the $^{235}$U concentration over the range $7{\cdot}2 \times 10^{-3}$ to $9{\cdot}2 \times 10^{-3}$ and amounts to 78 per cent of the radiation from natural uranium metal in the energy band 164–196 keV.

Fig. 2 shows the spectra from uranyl nitrate crystals with a $^{235}$U concentration of $4 \times 10^{-3}$, and from solutions containing different amounts of this salt. The background increases with the atomic stopping power of the source.

Fig. 3 shows the spectra from sources of different thickness of natural uranium metal; when the thickness of metal is less than the range of 2·3 MeV $\beta$-radiation caused by the daughter of $^{238}$U, the background decreases.

These experiments have shown that this background is the result of bremsstrahlung caused by $\beta$-radiation stopped in the source, and not to Compton background from high-energy $\gamma$-rays from $^{234}$Pa nor to a high-energy "tail" caused by poor resolution of the complex line at 100 keV.

The uranium salts and metal used in the experiments described were in equilibrium with the $\beta$-active daughter products $^{234}$Th and $^{234}$Pa. Spectra were also recorded from a freshly purified sample of $U_3O_8$, and it was found that the bremsstrahlung background increased as expected with the 24 day half-life of $^{234}$Th, as shown in Fig. 4.

*Conclusions*

The radiation at 184 keV from a sample of uranium is a mixture of radiation from $^{235}$U and bremsstrahlung. This bremsstrahlung results mainly from $\beta$-rays from $^{234}$Pa (a daughter of $^{238}$U) being stopped in the sample. The amount of bremsstrahlung, relative to the $^{235}$U line, depends on the $^{238}$U concentration and the size, nature and chemical history of the sample. Thus, at near natural level, measurement of the intensity of $\gamma$-radiation at 184 keV can only provide a good measure of $^{235}$U content when the daughter activity is removed (e.g. MEYER[5]) or when a correction for the background is applied (e.g. MORRISON and COSGROVE[21]). This correction is constant for samples of similar size and composition only when the daughters are in equilibrium; it is small for dilute solutions and for samples which are thin compared with the range of the $\beta$-rays.

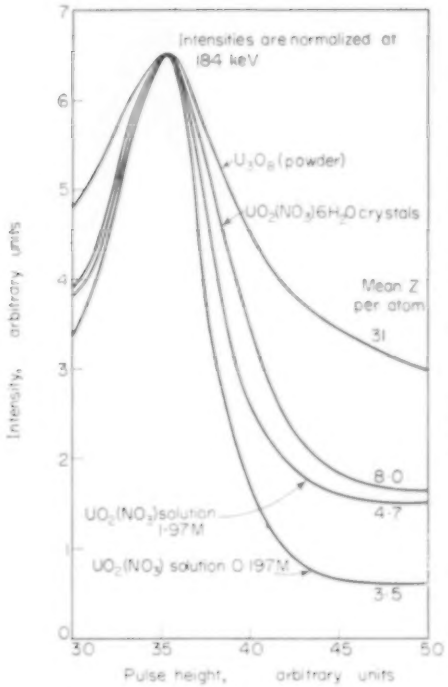



FIG. 2.—Gamma spectra of uranium compounds and solutions (0·43 %).

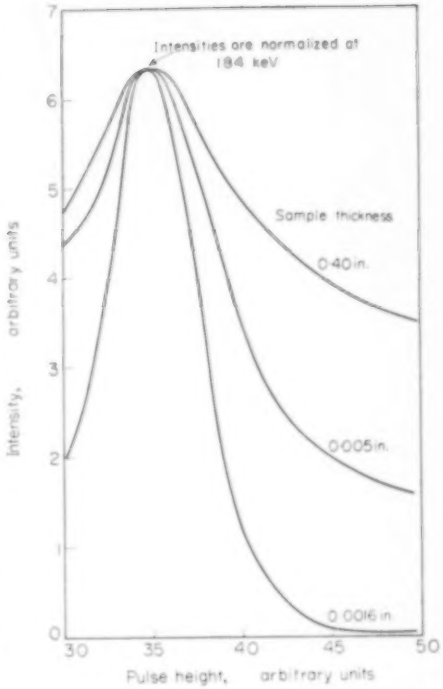



FIG. 3.—Variation of gamma spectrum of natural uranium metal with thickness of sample.

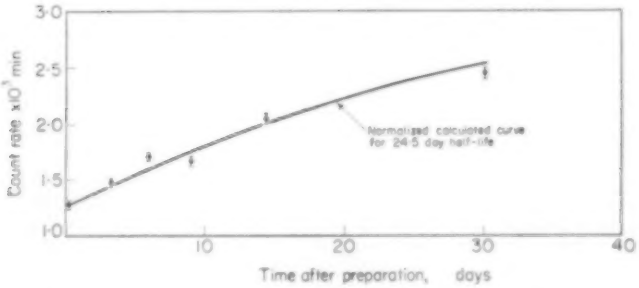



FIG. 4.—Growth of 184 keV line in freshly prepared $U_3O_8$ (channel width 164–196 keV).

*Acknowledgements*—This note is published by permission of Sir WILLIAM COOK, Managing Director, and Dr. H. KRONBERGER, Director of Research and Development of the United Kingdom Atomic Energy Authority (D. & E. Group).

Messrs. J. SHEPHERD, M. J. TODD and B. G. FERGUSON assisted with the experiments. Dr. A. N. HAMER prepared the sample of $U_3O_8$. Two pieces of uranium metal were prepared by Operations Branch, Springfields, of the U.K.A.E.A.

D. K. CARTWRIGHT
E. J. ROBBINS

*U.K.A.E.A. (Development & Engineering Group)*
*Research and Development Branch, Capenhurst, Chester*

Vol. 12 1959/6

## Unstable hydration of hydrochloric acid in tri-n-butyl phosphate

(*Received* 27 *October* 1959)

In earlier studies on the solute-solvent interaction in the system hydrochloric acid-water-tributyl phosphate,[1] (TBP), equal amounts of aqueous hydrochloric acid (of various concentrations) and of TBP were mixed together, the equilibrium phases were immediately separated, and the homogeneous organic phases were stored in a thermostat. After a few days it was observed that several of the homogeneous TBP phases had become heterogeneous; a second phase had been formed. The second layer, once formed, could not be returned to the organic phase. This phenomenon appeared in the above system when the initial aqueous hydrochloric acid concentration was ~6 N or higher. This observation prompted us to investigate this "dehydration" phenomenon more closely.

When studying the species formed in heterogeneous equilibrium between aqueous hydrochloric acid and pure TBP, we found that two well-defined species exist. The first, formed at lower initial aqueous acid concentrations, has the composition $[(Bu_3PO_4)_2{\cdot}HCl{\cdot}(H_2O)_6]$; the second, formed at higher initial acid concentrations in the aqueous phase, has the general formula $[Bu_3PO_4.HCl.(H_2O)_3]$. The first compound is formed completely when the initial aqueous acid concentration is ~6·3 N; as the acid concentration increases, the second compound is formed, the formation being complete at a concentration of ~10 N. Dehydration of the organic phase commences when the first compound is formed.

Five millilitres of 12·15 N hydrochloric acid and 5 ml of purified TBP were mixed together in a 10 ml centrifuge tube graduated to 0·1 ml and mechanically shaken for 15 min. Excellent phase separation was obtained after a few minutes' centrifugation and the menisci could be read to within ±0·025 ml. Equilibrations were carried out at 26 ± 1°C, and the stoppered tubes were kept in a thermostatic water bath at 26 ± 0·1°C. New samples were prepared every 4–6 days and were kept in the water bath. The decrease in volume of the TBP phase with time was followed by reading the menisci at intervals of a few days. After about 40 days the phases in the ten samples which had accumulated were simultaneously separated. In each case the TBP phase was analysed for its water content by the Karl Fischer reagent and the aqueous phase for its acid concentration.

Dehydration of the TBP layer is accompanied, as mentioned, by a decrease in its volume. Equilibration of equal volumes (5 ml) of concentrated HCl and TBP results in swelling of the TBP phase, giving 6·55 ml of the organic phase and 3·45 ml of the aqueous phase. Neglecting the extremely low solubility of TBP in aqueous hydrochloric acid,[2] the 6·55 ml of the organic layer contains 18·35 mmoles of TBP. After a period of about 30 days, when apparently no further change in volume takes place, the organic phase, initially 6·55 ml, had decreased in volume by ~0·35 ml, and the aqueous layer had increased by this volume from 3·45 to 3·80 ml. By a rough calculation, 0·35 ml corresponds to 18·3 mmoles of water. Thus, each mole of TBP releases 1 mole of water. The decrease in acid normality of the equilibrium aqueous phase (10 per cent) proves that the increase in volume of the aqueous layer (~10%) during the 30 day period is due exclusively to its dilution by pure water released from the equilibrium organic phase. The freshly-equilibrated organic layer contained ~56 mmoles of water, decreasing during a period of about 30 days to an apparently constant value of ~37 mmoles. The first value corresponds to approximately 3 moles of water per mole of TBP, and the second to a TBP : $H_2O$ ratio of two.

The fresh equilibrium organic layer contains the trihydrate of the TBP–HCl complex for a period of 2–3 days. Both trihydrate, dihydrate are present for the next three weeks, and finally after about thirty days only the dihydrate is present; this seems to be the stable hydrated form of the TBP–HCl complex.

We have found no example of such unstable hydration reported in the literature. Further evidence in agreement with the above finding has been obtained in work on the extraction of hydrobromic acid by TBP.[3]

Great caution is needed in drawing conclusions from the experimental results presented in this note. It is not yet clear whether this phenomenon represents a simple dehydration of the TBP–HCl trihydrate into the dihydrate (which might be related to differing stabilities of hydration by successive

[1] A. S. Kertes, *J. Inorg. Nucl. Chem.* In press.
[2] C. E. Higgins, W. H. Baldwin and B. A. Soldano, *J. Phys. Chem.* **63**, 113 (1959).
[3] A. S. Kertes and V. Kertes, *Canad. J. Chem.* In press.

water molecules in organic solvents under the conditions of heterogeneous equilibrium in solvent–solvent extraction processes), or whether it is the result of polymerization of the monomer molecules in the organic phase. A detailed examination of the problem is proceeding.

A. S. KERTES

*Department of Inorganic and Analytical Chemistry*
*The Hebrew University, Jerusalem, Israel*

---

## The Szilard–Chalmers reaction in *cis*- and *trans*-dichloro-bis-(ethylenediamine)-cobalt(III) nitrate*

(*Received* 29 *October* 1959)

WE have studied the chemical effects of the $^{59}Co(n, \gamma)^{60}Co$ and $^{37}Cl(n, \gamma)^{38}Cl$ reactions in the *cis* and *trans* isomers of crystalline $[Co(en)_2Cl_2]NO_3$. Samples were irradiated at dry-ice temperature, in the Brookhaven reactor, at a thermal neutron flux of $1{\cdot}1 \times 10^{13}$ $n/cm^2$ $sec^{-1}$ and a cadmium ratio of 38. All radioactivity measurements were made on liquid samples in a well-type scintillation counter with a NaI detector.

Samples for the study of $^{60}Co$ recoil species were irradiated in plastic containers for 5 min and stored in dry ice until the 10·5 min $^{60m}Co$ and 37·5 min $^{38}Cl$ had decayed. The percentage of the $^{60}Co$ found as *cis*- and as *trans*-$[Co(en)_2Cl_2]NO_3$ after irradiation of a given isomer was determined by a specific activity measurement. Samples of the *cis* and *trans* nitrates were isolated from a stock solution which contained the irradiated salt and carrier of the other isomer, and purified by fractional crystallization to constant specific activity. Concentrations of the two isomers in the stock and in solutions of the purified fractions were measured colorimetrically and aliquots of each solution were counted. The percentage of the $^{60}Co$ as $Co^{++}$ and forms exchangeable with $Co^{++}$ was determined by extracting a solution of the irradiated salt with 8-hydroxyquinoline. The results are shown in Table 1,

TABLE 1.—DISTRIBUTION OF $^{60}Co$

| Target compound | Post-irradiation treatment | % as parent isomer | % as other isomer | % as $Co^{++}$ |
|---|---|---|---|---|
| *cis*-$[Co(en)_2Cl_2]NO_3$ | none | 3·1 ± 0·1 | 0·1 | 88·9 ± 0·3 |
| *trans*-$[Co(en)_2Cl_2]NO_3$ | none | 7·3 ± 0·5 | 0·2 | 82·3 ± 0·4 |
| *cis*-$[Co(en)_2Cl_2]NO_3$ | annealed 1 hr at 100°C | 42·9 ± 1·3 | 0·1 | — |
| *trans*-$[Co(en)_2Cl_2]NO_3$ | annealed 1 hr at 100°C | 48·0 ± 2·1 | 0·1 | — |

where "% as other isomer" refers to the activity found in the *trans* form when the *cis* salt was irradiated, and vice versa. The errors quoted are average deviations.

Samples for $^{38}Cl$ recoil study were irradiated for 10 sec and the percentage of the $^{38}Cl$ as the parent compound determined by the methods above, with the modification that aliquots for counting were treated with hydrogen sulphide to decompose complex ions and remove as the sulphide all interfering cobalt activity. Exchange between the complex ions and chloride ion should not occur under these conditions.[1] The percentage of the $^{38}Cl$ as chloride ion was measured by passing a solution of the irradiated salt through a cation exchange resin under conditions which minimized aquation of the complex ion. Silver chloride was precipitated in the effluent and carried down virtually all of the anionic $^{38}Cl$. The results of these experiments are shown in Table 2. The effect of post-irradiation annealing was studied with samples irradiated in quartz ampoules, heated at

* Research performed under the auspices of the U.S. Atomic Energy Commission.

[1] G. W. ETTLE and C. H. JOHNSON, *J. Chem. Soc.* 1490 (1940).

Vol. 12 1959/6

100°C for 1 hr by immersion in boiling water, and analysed for activity in the *cis* and *trans* forms. These data are also shown in Tables 1 and 2.

These results permit comparisons between the recoil behaviour of a hexa-co-ordinated central atom and a univalent ligand atom in the same target molecule, as well as comparisons between two structural isomers of the same compound. Several interesting features can be seen from the data. The percentage of the total activity in the parent form, the *retention*, is distinctly larger for $^{38}$Cl than

TABLE 2.—DISTRIBUTION OF $^{38}$Cl

| Target compound | Post-irradiation treatment | % as parent isomer | % as other isomer | % as $Cl^-$ |
|---|---|---|---|---|
| *cis*-$[Co(en)_2Cl_2]NO_3$ | none | 12·5 ± 0·1 | 0·4 | 82·1 ± 0·9 |
| *trans*-$[Co(en)_2Cl_2]NO_3$ | none | 15·5 ± 0·4 | 0·7 | 79·8 ± 1·6 |
| *cis*-$[Co(en)_2Cl_2]NO_3$ | annealed 1 hr at 100°C | 67·9 ± 1·2 | 0·3 | — |
| *trans*-$[Co(en)_2Cl_2]NO_3$ | annealed 1 hr at 100°C | 70·1 ± 1·3 | 0·4 | — |

for $^{60}$Co, in both *cis* and *trans* targets. Since bond rupture should be more favourable for $^{38}$Cl recoils, the data demonstrate that retention of activity for both $^{60}$Co and $^{38}$Cl must be due to secondary processes rather than any failure of the target molecule to rupture. For both $^{60}$Co and $^{38}$Cl the retentions for *trans* targets are greater than those for *cis*, while the percentage of the activity in the unco-ordinated form is in the reverse order.

Perhaps the most significant result is that there is very little $^{60}$Co or $^{38}$Cl which appears in the other isomeric form for either *cis* or *trans* targets. The data for the yields in the other isomeric forms are all based on low counting rates and the true values are probably closer to zero than the data would indicate. This result is similar to that obtained by ZUBER,[2] who irradiated *d*-$[Co(en)_3](NO_3)_3$ and found the yield of $^{60}$Co to be 4·5 per cent in the dextro form and 0·5 per cent in the laevo form.

The data on the annealed samples show marked increases in retention but no significant increases in the activity as the other isomeric form. The changes in the retention of $^{60}$Co were 39·8 ± 1·3 per cent and 40·7 ± 2·1 per cent for *cis* and *trans* targets respectively, while those of $^{38}$Cl were 55·4 ± 1·2 per cent and 54·6 ± 1·3 per cent.

It is evident from these results that the post-irradiation process by which activity is incorporated into the parent chemical form, which clearly requires thermal activation, exhibits the same isomeric specificity as the corresponding process occurring during the slowing down of the hot atom. This common specificity suggests that there may not be a sharp distinction between the two types of process and that similar factors may control both. HARBOTTLE and SUTIN[3] have recently proposed the "hot-zone" model of recoil processes which attempts to describe both initial recoil and subsequent annealing reactions. This model, in which each recoil atom is thought to produce atomic displacements and a high transient temperature in a small region of the crystal, regards the annealing reactions as the continuation of processes which are quenched by the rapid cooling of the hot zone. The stereospecificity mentioned above would seem to confirm this view. A stereospecific factor for both the initial and post-irradiation reactions is provided by the undisturbed crystalline phase surrounding the recoil site. This phase could serve as a template for the formation of radioactive parent molecules in the bulk configuration and prevent its formation as the other isomer, provided the reactions that form the parent compound occur at energies low enough to reflect the different stabilities of the *cis* and *trans* isomers in a given lattice.

H. E. RAUSCHER
N. SUTIN
J. M. MILLER

*Departments of Chemistry, Brookhaven National Laboratory Upton, L.I., N.Y. Columbia University, New York, N.Y.*

[2] A. V. ZUBER, NYO-6142 (1954).
[3] G. HARBOTTLE and N. SUTIN, *J. Phys. Chem.* **62**, 1344 (1958); *Advances in Inorganic and Radiochemistry* Vol. I, p. 369. Academic Press, New York (1959).

## The convenient laboratory preparation of borazole

(*Received* 11 *November* 1959)

THE chemistry of $B_3N_3H_6$, borazole, has received an ever increasing attention since its discovery by STOCK in 1926. STOCK's original preparation from ammonia and diborane requires use of high vacuum techniques and consequently lacks general utility.[1] Thermal decomposition of a mixture of $LiBH_4$ or $NaBH_4$ with $NH_4Cl$ is somewhat better but is difficult to use for large preparations owing to simultaneous formation of significant amounts of diborane as a by product.[2] More recently reduction of B-trichloroborazole with $LiBH_4$ or $NaBH_4$ in various solvents has proved to be convenient.[3,4] The formation of 1·5 moles of $B_2H_6$ per mole of $B_3Cl_3N_3H_3$ used, necessitates special precautions and makes the reaction difficult to use on a large scale. A modification of this reaction which avoids these difficulties is described in the present paper.

Neither borazole nor B-trichloroborazole react rapidly with tertiary aliphatic amines at room temperature or below. Simple incorporation of a suitable amine in the solvent results in a procedure no more difficult than those normally used for handling somewhat moisture-sensitive substances, presumably by reacting rapidly and completely *in situ* with the diborane as it is liberated.

### *Experimental*

The B-trichloroborazole used in this investigation was prepared by reaction of ammonium chloride with boron trichloride at 200°C.[5] The sample used in this investigation was prepared by Mr. GERALD BRENNAN in 1957 and had been stored in a 2 l. stoppered flask without additional protection since that time. Sublimation of a portion of it showed the sample to still be of greater than 99 per cent purity. Commercial sodium borohydride was used without further purification. The dimethyl ether of diethylene glycol (diglyme) was refluxed over calcium hydride and subsequently distilled from lithium aluminum hydride. Commercial tri-n-butylamine was refluxed with acetic anhydride and distilled at atmospheric pressure.

In a typical preparation, a 2 l., three-neck flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel was charged with 77 g of $NaBH_4$ dissolved in about 600 cm³ of diglyme. The flask was chilled to 0° and 380 g (about 25 per cent excess) of tri-n-butylamine were added with vigorous stirring. The reaction flask was flushed with a slow stream of dry nitrogen and a solution of 100 g of $B_3Cl_3N_3H_3$ in 250 cm³ of diglyme was added to the flask dropwise over a 1 hr period. The stirring was continued for 30 min after the addition was complete.

The reaction flask was attached to a spiral reflux condenser, cooled with a salt-ice bath, and the reaction mixture distilled under high vacuum, first at room temperature and later with gentle heating to 40–50°. Borazole and some ether collected in a dry ice-cooled trap. The crude borazole was transferred to a Podbielniak distillation column which had been previously flushed with nitrogen. The cold finger in the distilling head was cooled with circulating brine and the mixture distilled at atmospheric pressure. The receiving flask was cooled with an ice-bath and a fraction of 20·3 g (corresponding to approximately a 46 per cent yield) boiling at 54·5° was collected. The vapour pressure of this fraction was 86 mm at 0° compared to 85 mm for pure borazole. A gas chromatogram showed one additional component to be present to the extent of less than one percent. Mass spectrometric investigation of the impurity (separated by conventional vacuum line techniques) failed to identify the component but showed it to be boron-free. Infra-red examination shows the substance to contain carbon–hydrogen bonds and the material apparently arises from ether cleavage.

### *Discussion*

Tri-n-butylamine was chosen for this preparation since it was a high boiling, aliphatic, tertiary amine available from stock. In preliminary investigations triethylamine was used and worked

[1] A. STOCK and E. POHLAND, *Ber.* **49B**, 2215 (1926).
[2] G. W. SCHAEFFER, R. SCHAEFFER and H. I. SCHLESSINGER, *J. Amer. Chem. Soc.* **73**, 1612 (1951).
[3] R. SCHAEFFER *et al.*, *J. Amer. Chem. Soc.* **76**, 3303 (1954).
[4] L. HOHNSTEDT, *Abstracts of Papers presented at the 133rd Meeting of the American Chemical Society in San Francisco, April*, 1958.
[5] C. A. BROWN and A. W. LAUBERGAYER, *J. Amer. Chem. Soc.* **77**, 3699 (1955). See also G. BRENNAN, M.S. thesis, Iowa State University, 1957. This compound is now available in developmental quantities from the U.S. Borax Research Corporation.

Vol. 12 1959/6

satisfactorily but proved difficult to remove completely from the desired product. Other suitable amines could no doubt be substituted.

For large scale preparation, recovery of the amine borane and reconversion to free amine and sodium borohydride by treatment with sodium hydride might be worthwhile.[6] The net reaction in that event corresponds to reduction of the haloborazole wtih sodium hydride.

*Acknowledgement*—The authors gratefully acknowledge the financial support of the National Science Foundation Grant No. G 6224 which made this investigation possible.

GERD H. DAHL
RILEY SCHAEFFER

*Dept. of Chemistry, Indiana University*
*Contribution No.* 918
*Bloomington, Indiana*

[6] R. KÖESTER, *Angew. Chem.* **69**, 94 (1957).

Vol.
12
9/60

J. Inorg. Nucl. Chem., 1960, Vol. 12, pp. 382 to 384. Pergamon Press Ltd. Printed in Northern Ireland

# LETTERS TO THE EDITOR

## The decomposition of nitric acid co-extracted with uranyl nitrate into tributyl phosphate

(*Received* 13 *August* 1959)

THE co-extraction of nitric acid and uranyl nitrate by tributyl phosphate (TBP) was reported in a previous paper.[1] It is often observed that when the nitric acid co-extracted with uranyl nitrate is kept in the organic phase without back-extraction, the nitric acid gradually decomposes. This phenomenon is investigated in the present study.

Extractions were carried out at 20°C in the manner described in the earlier paper.[2] Afterwards, the organic phase was separated from the aqueous one, and kept at 20°C in the light. After a definite time the total amount of nitric acid in the organic phase was determined with the method reported in a previous paper.[1] The percentage decomposed is expressed as $(C_1-C_2/C_1) \times 100$, where $C_1$ is the initial nitric acid concentration in the organic phase and $C_2$ is the concentration found after storage.

Table 1 shows the decomposition behaviour of the extracted nitric acid during storage in light. In this case a solution of 5 g/l. of uranyl nitrate was extracted with TBP solutions in kerosene.

TABLE 1

| TBP conc. (%) | $HNO_3$ conc. (M) (original aq.) | Percentage decomposed after | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 day | 3 days | 7 days | 15 days | 30 days | 60 days |
| 0 | 13 | 0 | 0 | 0 | 0 | 0 | 0 |
| 19 | 13 | 12·1 | 17·8 | 22·2 | 37·0 | 40·0 | 44·6 |
| 39 | 3 | 0 | 0 | 0 | 0 | 0 | 0 |
| 39 | 6 | 0 | 0 | 0 | 0 | 0 | 0 |
| 39 | 9 | 0·14 | 0·35 | 0·40 | 0·42 | 0·65 | 0·70 |
| 39 | 13 | 5·32 | 15·9 | 20·6 | 27·8 | 32·5 | 33·0 |
| 58 | 13 | 5·96 | 9·25 | 12·5 | 15·8 | 17·5 | 17·5 |
| 97 | 13 | 0 | 0 | 0 | 0 | 0 | 0 |

From Table 1 it is observed that the percentage of nitric acid decomposed increases at higher acidities of the original aqueous phase and lower TBP concentrations of the organic phase. It may be caused by the nitric acid being extracted into the organic phase (from the aqueous phase) beyond the formation of the $HNO_3$·TBP complex at high acidities.[2] And the decomposition of nitric acid attains to an approximate equilibrium after storage for about one month. The data presented in Table 2 were obtained in order to investigate the effect of the presence of uranyl nitrate on the decomposition of nitric acid. In this case solutions of 0, 1, 5, and 10 g/l. of uranyl nitrate were extracted with 19 per cent TBP with varying concentrations of nitric acid. After extraction, these organic phases were kept in light for two months.

From Table 2 it is seen that the presence of uranyl nitrate increases the decomposition of the

[1] T. SATO, *J. Inorg. Nucl. Chem.* **9**, 188 (1959).
[2] T. SATO, *J. Inorg. Nucl. Chem.* **6**, 334 (1958).



Vol. 12 1959/6

TABLE 2

| $HNO_3$ conc. (M) (original aq.) | Percentage decomposed | | | |
|---|---|---|---|---|
| | 0 g/l.* | 1 g/l.* | 5 g/l.* | 10 g/l.* |
| 1 | 0 | 0 | 0·10 | 0·20 |
| 3 | 0 | 0·10 | 0·35 | 0·50 |
| 5 | 0·35 | 0·54 | 0·65 | 0·80 |
| 6 | 0·90 | 1·06 | 1·27 | 1·35 |
| 7 | 1·01 | 1·44 | 1·81 | 2·07 |
| 9 | 1·87 | 3·88 | 5·40 | 7·13 |
| 11 | 3·00 | 8·75 | 10·0 | 11·7 |
| 13 | 25·6 | 38·2 | 44·6 | 55·0 |

* Initial concentrations of aqueous uranyl nitrate solutions

nitric acid co-extracted into the organic phase. This phenomenon may mean that the $UO_2(NO_3)_2 \cdot 2TBP$ complex is stronger than that of $HNO_3 \cdot TBP$.[3] However, it is possible that the decomposition of nitric acid is due to reduction by uranium (IV) resulting from the photochemical reduction of uranium (VI) in the organic solvent.[4]

*Acknowledgement*—The author thanks Mr. T. GOTO of our Institute for assistance with the experimental work.

TAICHI SATO*

*Government Chemical Industrial Research Institute*
*Hatagaya, Shibuya-ku*
*Tokyo*

* Present address: Department of Chemistry, The University, Sheffield 10.

[3] T. SATO, *J. Inorg. Nucl. Chem.* **7**, 148 (1958).
[4] C. F. BAES, A. ZINGARO and C. F. COLEMAN, *J. Phys. Chem.* **62**, 129 (1958).

## The chemistry of decaborane II iodination in solvent[1,2]

(*Received* 6 *November* 1959)

THE reported method[1,3] for iodinating decaborane, heating iodine and decaborane in a sealed tube, does not conveniently lend itself to large scale preparation and the subsequently facilitated study of the reactions of the iododecaboranes. For this reason, iodination in solvent was attempted.

Only an insignificant amount of iodination could be effected in hydrocarbon solvents at 100° even at high concentrations of decaborane and iodine. This was surprising since it was noticed that the solventless reaction in a sealed tube took place only above the melting point of decaborane; that is, in the liquid state. However, when equimolar quantities of iodine, freshly recrystallized decaborane and aluminium chloride were refluxed in carbon disulphide for 8 hr, the reaction proceeded smoothly and completely. The crude product contained no diiododecaborane according to the mass spectrum[4] and consisted of 2-iododecaborane and 5-iododecaborane in the ratios of 65–35 according to infra-red analysis[5] which is the same as that reported for direct iodination.[1]

[1] For previous paper see M. HILLMAN, *Abstracts of the Meeting of the 135th American Chemical Society Boston, Mass., April* 1959. p. 44-M; *J. Amer. Chem. Soc.* In press.
[2] This work was supported by Air Force Contract 33(600)-33920.
[3] A. STOCK, *Hydrides of Boron and Silicon.* Cornell University Press, Ithaca (1933).
[4] We are indebted to Dr. J. H. NORMAN of these laboratories and his staff for the mass spectrum.
[5] We are indebted to Miss D. M. ROBINS of these laboratories for the quantitative infra-red analysis.

That such widely divergent conditions (sealed tube, high temperature, no solvent and solvent, catalyst, low temperature) should give the same ratio of isomers indicated that the possibility of the two isomers being formed by different mechanisms is remote. The reaction forming both isomers is apparently the attack of a positive iodine ion on an electron-rich centre. For the 5 position to be electron-rich, even secondary to the 2 position, is contrary to LIPSCOMB's[6] analysis of the molecule which placed positive charges on the 5 position. However, LIPSCOMB's original analysis did not take the bridge hydrogens into account. More recent work[7] apparently amending the previous approximations places the positive charges on the 6 and 9 positions. The 5 position might then have electrons available for an attack of an electrophilic reagent to the relative extent indicated by the ratios of isomers formed.

M. HILLMAN*

*Energy Division*
*Olin Mathieson Chemical Corporation*
*Niagara Falls, New York*

* Present address: Hot Laboratory, Brookhaven National Laboratory, Upton, Long Island, N.Y

[6] W. H. EBERHARDT, B. CRAWFORD and W. N. LIPSCOMB, *J. Chem. Phys.* **22**, 989 (1954).
[7] W. N. LIPSCOMB, AEC publication NP6912; see also W. N. LIPSCOMB and J. VAN DER MAAS REDDY, *J. Amer. Chem. Soc.* **81**, 754 (1959).

Vol.
12
1959/

J. Inorg. Nucl. Chem., 1960, Vol. 12, p. 385. Pergamon Press Ltd. Printed in Northern Ireland

# ANNOUNCEMENT

THE *ORNL Master Analytical Manual*, which may be of interest to analytical chemists, is now available in reprinted form. The *Manual* is a collection of the analytical methods that are in use in the Analytical Chemistry Division of the Oak Ridge National Laboratory. The reprinted form of the *Manual* can be purchased from the Office of Technical Services, Department of Commerce, Washington 25, D.C., in the following form

| Section | Methods |
|---|---|
| 1 | Ionic |
| 2 | Radiochemical |
| 3* | Spectrographic |
| 5* | Nuclear Analyses |
| 9 | Process |

* Sections 3 and 5 are bound together. The Table of Contents for the complete *Manual* is bound with the separate sections.

Annual supplements are issued to the *Manual*; these will also be available from the Office of Technical Services.

Vol.
12
59/60

J. Inorg. Nucl. Chem., 1960, Vol. 12, p. 386. Pergamon Press Ltd. Printed in Northern Ireland

## ERRATUM

F. A. COTTON and G. W. GEORGE: Properties of $SF_4$ and Its Adduct with $BF_3$. *J. Inorg. Nucl. Chem.* **7,** 397 (1958).

SEEL and DETMER[1] have recently reported that $[SF_3^+BF_4^-]$ vaporizes to $SF_{4(g)} + BF_{3(g)}$ with an enthalpy of vaporization of 25·5 kcal/mole. Our van't Hoff equation[2] ($\log p = 12{\cdot}8 - 3230/T$) differs somewhat from theirs ($\log p = 11{\cdot}34 - 2783/T$). Our van't Hoff equation gives a $\Delta H$ of $29{\cdot}6 \pm 2$ kcal/mole, not $14{\cdot}8 \pm 1$ kcal/mole as we incorrectly reported.[2] Similarly, the data of SHEFT, MARTIN and KATZ[3] for $[BrF_2^+SbF_6^-]_{(s)} = BrF_{3(g)} + SbF_{5(g)}$ were incorrectly treated by us. The correct enthalpy of vaporization, 27·8 kcal/mole, obtainable from their data is twice the value (13·9 kcal/mole) we reported.

[1] F. SEEL and O. DETMER, *Z. Anorg. Chem.* **301,** 113 (1959).
[2] F. A. COTTON and J. W. GEORGE, *J. Inorg. Nucl. Chem.* **7,** 397 (1958).
[3] I. SHEFT, A. F. MARTIN and J. J. KATZ, *J. Amer. Chem. Soc.* **78,** 1557 (1956).

Vol.
12
1959/6

ol.
12
9/60

END